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STYRENE

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substance. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

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STYRENE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

December 1984

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

STYRENE ($C_6H_5CH:CH_2$)

Colourless liquid with a disagreeable aromatic odour

SYNONYMS

Vinylbenzene, Vinylbenzol, Cinnamene, Cinnamenol, Styrol, Phenylethylene, Phenylethane

IDENTIFICATION NUMBERS

UN No. 2055 (inhibited); CAS No. 100-42-5; OHM-TADS No. 7216911; STCC No. 4907265

GRADES & PURITIES

Commercial or polymerization, 99.5 or 99.6 percent, containing the inhibitor para-tert-butylcatechol

IMMEDIATE CONCERNS

Fire: Flammable. Flashback may occur along vapour trail. At elevated temperatures, polymerization may occur

Human Health: Moderate toxicity by inhalation or ingestion

Environmental: Harmful to aquatic life in low concentrations

PHYSICAL PROPERTY DATA

State: (15°C, 1 atm): liquid
Boiling Point: 145.2°C
Freezing Point: -30.6°C
Flammability: flammable
Flash Point: 32°C (CC)
Vapour Pressure: 0.6 kPa (20°C)
Density: 0.906 g/mL (25°C)

Solubility (in water): 0.3 g/100 mL (25°C)
Behaviour (in water): floats; no reaction
Behaviour (in air): vapour is heavier than air
Odour Threshold Range: 0.05 to 0.15 ppm
Polymerization: occurs if heated, exposed to catalytic materials, or if inhibitor depleted

ENVIRONMENTAL CONCERNS

Styrene is toxic to aquatic life at concentrations as low as 20 mg/L. It accumulates in fish and produces tainting of flesh.

HUMAN HEALTH

TLV: 50 ppm (215 mg/m^3)

IDLH: 5000 ppm

Exposure Effects

Inhalation: Inhalation causes irritation to mucous membranes, difficult breathing, coughing, dizziness, fatigue, and loss of consciousness

Contact: Prolonged or repeated skin contact may cause moderate irritation. Eye contact produces drying and cracking, irritation, and slow-to-heal corneal injury

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Do not extinguish fire unless release can be stopped. Use foam, dry chemical, carbon dioxide, or water fog to extinguish. Cool fire-exposed containers with water. Stay clear of tank ends.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Adsorb residual liquid on natural or synthetic sorbents (noncombustible), shovel into covered containers

Water: Contain with booms, weirs or natural barriers. Use (oil) skimming equipment or suction hoses to remove slick, followed by the application of sorbents to remove final traces

Air: Use water spray to disperse flammable vapour. Control runoff for later treatment and/or disposal

NAS HAZARD RATING

Category	Rating
Fire	3
Health	
Vapour Irritant	2
Liquid or Solid Irritant	2
Poison	2
Water Pollution	
Human Toxicity	1
Aquatic Toxicity	3
Aesthetic Effect	2
Reactivity	
Other Chemicals	2
Water	0
Self-reaction	3

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless, oily liquid (Dow MSDS 1979)
Usual shipping state	Liquid; inhibited with para-tert-butylcatechol (Dow MSDS 1979)
Physical state at 15°C, 1 atm	Liquid
Freezing point	-30.6°C (Kirk-Othmer 1983)
Boiling point	145.2°C (CRC 1980; TAB 1981)
Vapour pressure	0.60 kPa (20°C) (Kirk-Othmer 1983)

Densities

Density	Liquid: 0.9059 g/mL (20°C) (Kirk-Othmer 1983) Vapour: 0.280 g/L (15°C) (Verschueren 1984)
Specific gravity	Liquid: 0.9044 (25°/25°C) (water = 1) (Dow MSDS 1979) Vapour: 3.6 (air = 1) (Dow MSDS 1979)

Fire Properties

Flammability	Flammable liquid (NFPA 1978)
Flash point	
CC	32°C (NFPA 1978),
OC	31.1°C-34.4°C (Kirk-Othmer 1983)
Autoignition temperature	490°C (NFPA 1978)
Burning rate	5.2 mm/min (CHRIS 1978)
Upper flammability limit	6.1 percent (v/v) (NFPA 1978)
Lower flammability limit	1.1 percent (v/v) (NFPA 1978) 0.9 percent (v/v) (Dow 1981)
Heat of combustion	4263 kJ/mole (25°C) (Kirk-Othmer 1983)
Combustion products	Carbon dioxide and water (CRC 1980)
Flashback potential	Vapour may travel considerable distance to source of ignition and flash back (NFPA 1978)
Behaviour in a fire	At elevated temperatures, uncontrolled polymerization may take place (NFPA 1978). Styrene monomer vapours are uninhibited and

	may form polymers in vents and containers, causing stoppages (NFPA 1978)
Electrical ignition hazard	May be ignited by static discharge
Other Properties	
Molecular weight of pure substance	104.16 (CRC 1980)
Constituent components of typical commercial grade	99.6 percent styrene with 55 ppm, max. para-tert-butylcathechol as inhibitor (Dow MSDS 1979)
Refractive index	1.5468 (20°C) (CRC 1980)
Viscosity	0.763 mPa•s (20°C) (Kirk-Othmer 1983)
Liquid interfacial tension with air	30.86 mN/m (20°C) (Kirk-Othmer 1983)
Liquid interfacial tension with water	35.48 mN/m (19°C) (CHRIS 1978)
Latent heat of fusion	10.95 kJ/mole (at melting point) (Lange's Handbook 1979)
Latent heat of sublimation	43.9 kJ/mole (25°C) (Lange's Handbook 1979)
Latent heat of vaporization	44.6 kJ/mole (25°C), 36.9 kJ/mole (145°C) (Kirk-Othmer 1983)
Heat of formation	-103.8 kJ/mole (25°C) (Sussex 1977)
Ionization potential	8.42 eV (Rabalais 1972)
Heat of polymerization	74.48 kJ/mole (Kirk-Othmer 1983)
Volumetric shrinkage on polymerization	17 percent (Kirk-Othmer 1983)
Cubical coefficient of expansion	9.71×10^{4} (20°C) (Kirk-Othmer 1983)
Antoine vapour pressure equation	Log_{10} P = 6.08201 - (1445.58/(209.43 + T)) (P = kPa, T = °C) (Kirk-Othmer 1983)
Heat capacity	
Constant pressure (Cp)	Liquid: 1.690 J/(g•K) (20°C) (Kirk-Othmer 1980) Vapour: 1.179 J/(g•K) (25°C) (Kirk-Othmer 1980)
Critical pressure	3810 kPa (Kirk-Othmer 1983)
Critical temperature	369°C (Kirk-Othmer 1983)
Saturation concentration	31 g/m^3 (20°C), 52 g/m^3 (30°C) (Verschueren 1984)

Log_{10} octanol/water partition coefficient	2.95 (Hansch and Leo 1979)
Evaporation rate	0.13 g/(m^2s) (20°C, wind 4.5 m/s) (this work)
Solubility	
In water	0.028 g/100 mL (15°C), 0.04 g/100 mL (40°C) (Verschueren 1984) 0.03 g/100 mL (25°C) (Kirk-Othmer 1983). (Note: Water is soluble in styrene to the extent of 0.07 g/100 mL at 25°C (Kirk-Othmer 1983))
In other common materials	Soluble in methanol and carbon disulphide (CRC 1980). Infinitely soluble in acetone, carbon tetrachloride, benzene, ether, n-heptane and ethanol (Kirk-Othmer 1983)
Vapour Weight to Volume Conversion Factor	1 ppm = 4.323 mg/m^3 (20°C) (Verschueren 1984)

Polymerization Behaviour

Pure styrene polymerizes slowly at room temperature and more rapidly at elevated temperatures. The heat released by polymerization (heat of polymerization) is quite large: once polymerization is initiated, the process can become self-accelerating. Once initiated, the temperature can approach 300°C during runaway polymerization. This temperature increase can lead to high pressure increases in a closed container. Even a small container of about 1 litre showed a 20-30°C temperature rise; a 4 litre container showed a 100-200°C temperature rise during runaway polymerization (Brighton 1979; Dow 1981).

TBC (p-t-butylcatechol) is universally used as a polymerization inhibitor at levels of 10 to 60 ppm. TBC slowly converts to quinone and is thus slowly depleted. It has been shown that samples containing 6-8 ppm TBC are not adequately protected against polymerization. To be effective, TBC requires the presence of dissolved oxygen. The effect of inhibitor and oxygen on the shelf life (i.e., before polymerization is possible) is estimated to be as follows (Dow 1981):

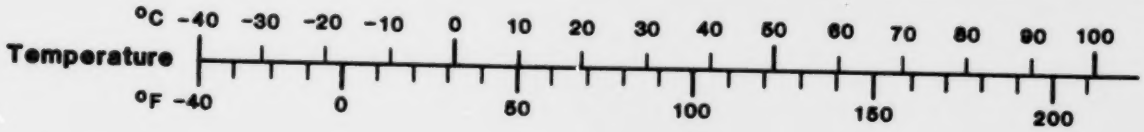
	12 ppm TBC		50 ppm TBC
Temperature	Oxygen Saturated	Low Oxygen (>3 ppm)	Oxygen Saturated
15°C	6 mo	10-15 d	> 1 yr
30°C	3 mo	4-5 d	3-4 mo
43°C	8-12 d	< 1 d	< 30 d

Polymerization can be initiated (with or without TBC) by a number of catalysts such as acids, bases, etc. Polymerization could also be initiated in a spill situation by contact with soil if all other conditions are sufficient (Santodonato 1980).

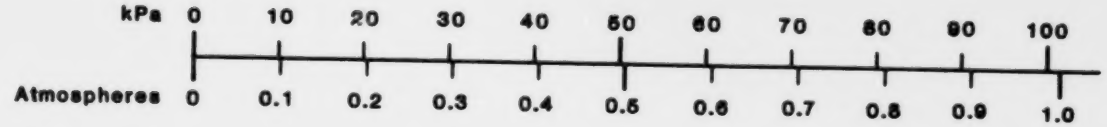
TABLE 1

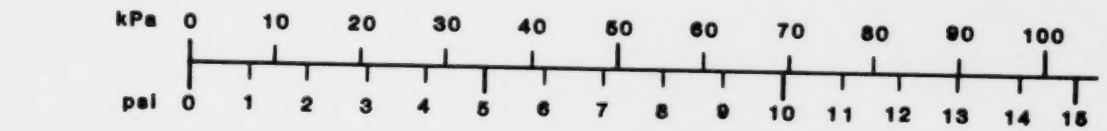
STYRENE

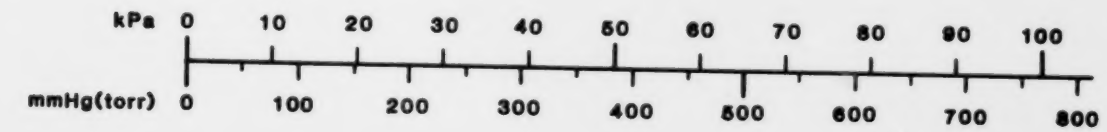
CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa







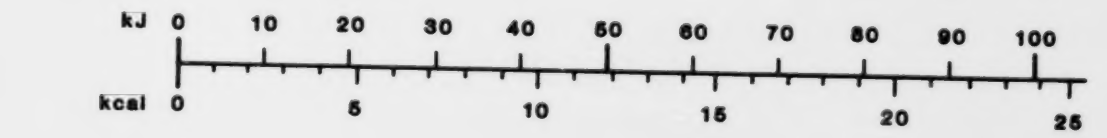
Viscosity

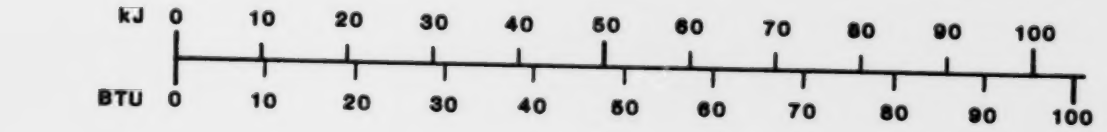
Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)
1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1,000 J





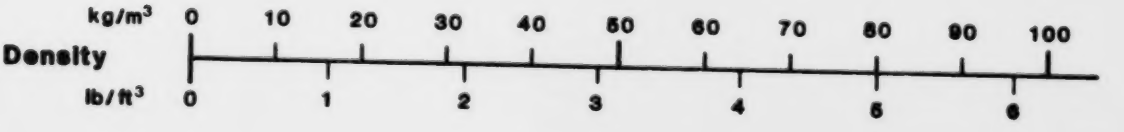


Figure 1

STYRENE

Vapour Pressure vs Temperature

Reference: Chem.Eng. 1976

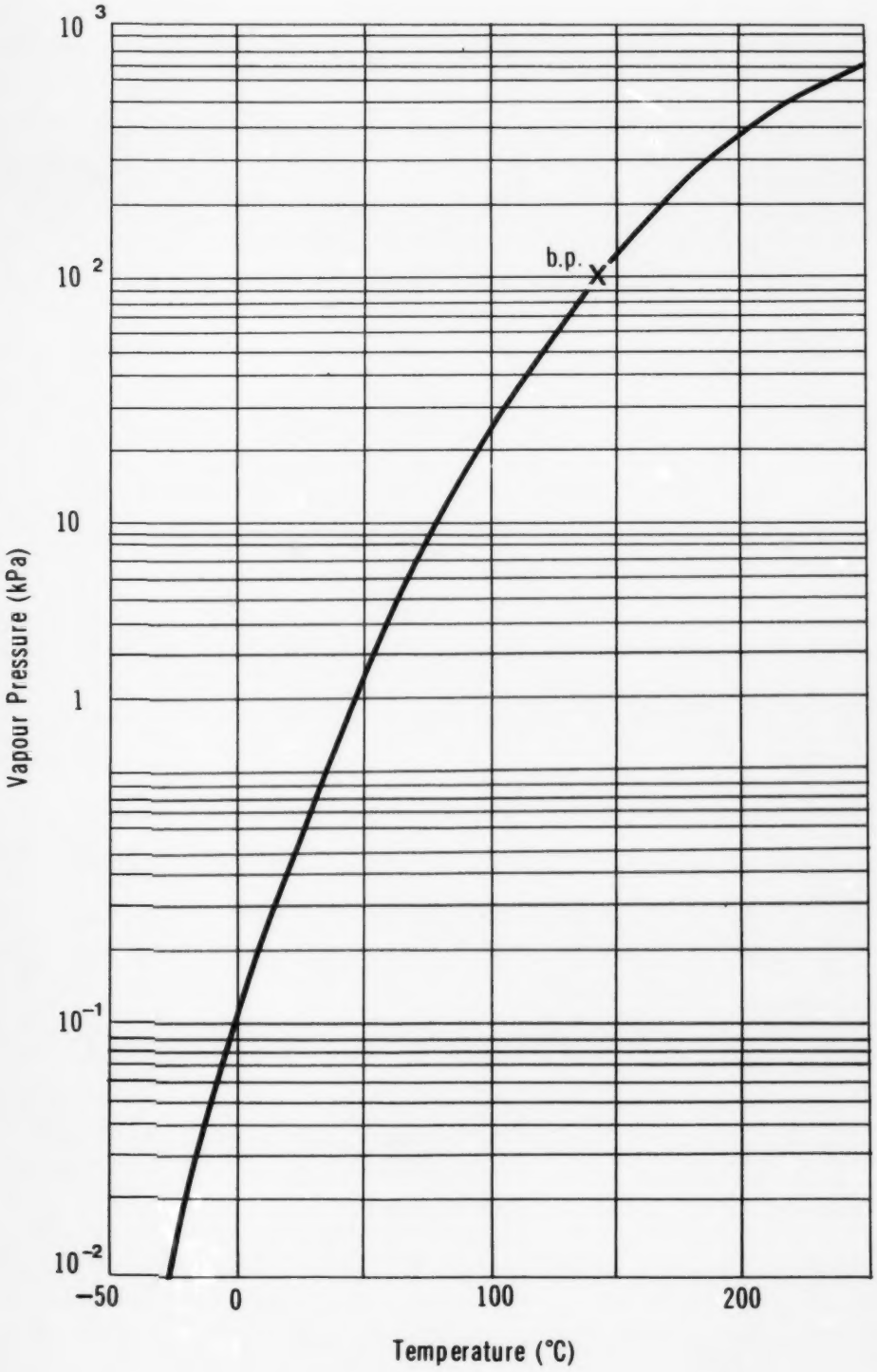


Figure 2

STYRENE

LIQUID DENSITY VS TEMPERATURE

Reference: Chem.Eng. 1976

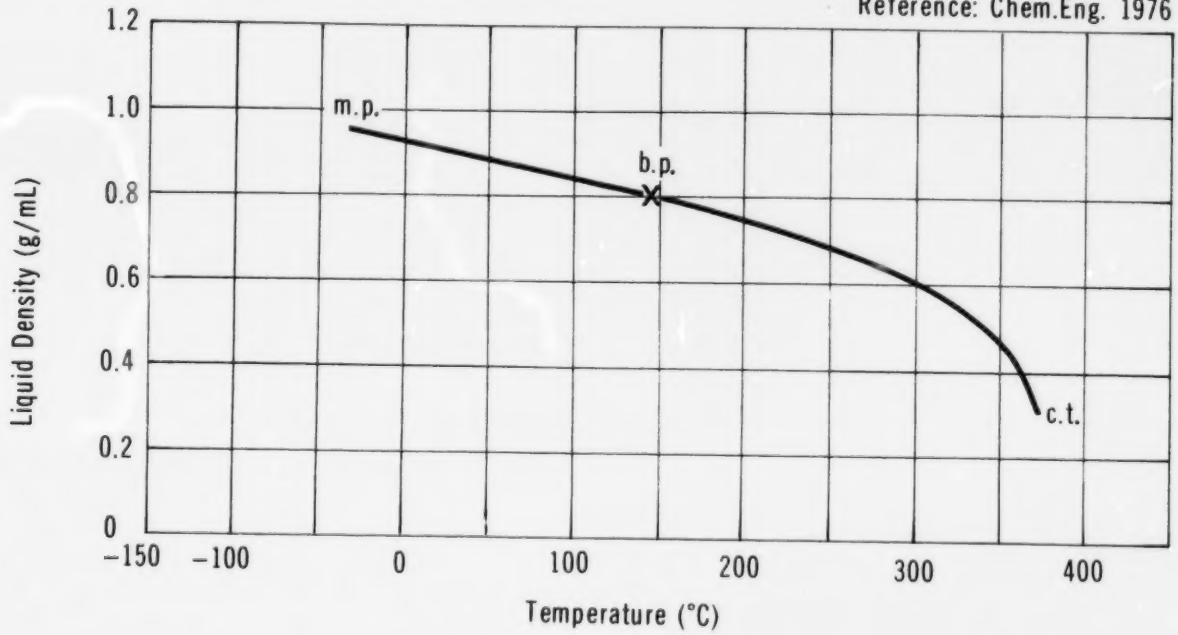


FIGURE 3

STYRENE (UNINHIBITED)

POLYMERIZATION RATE

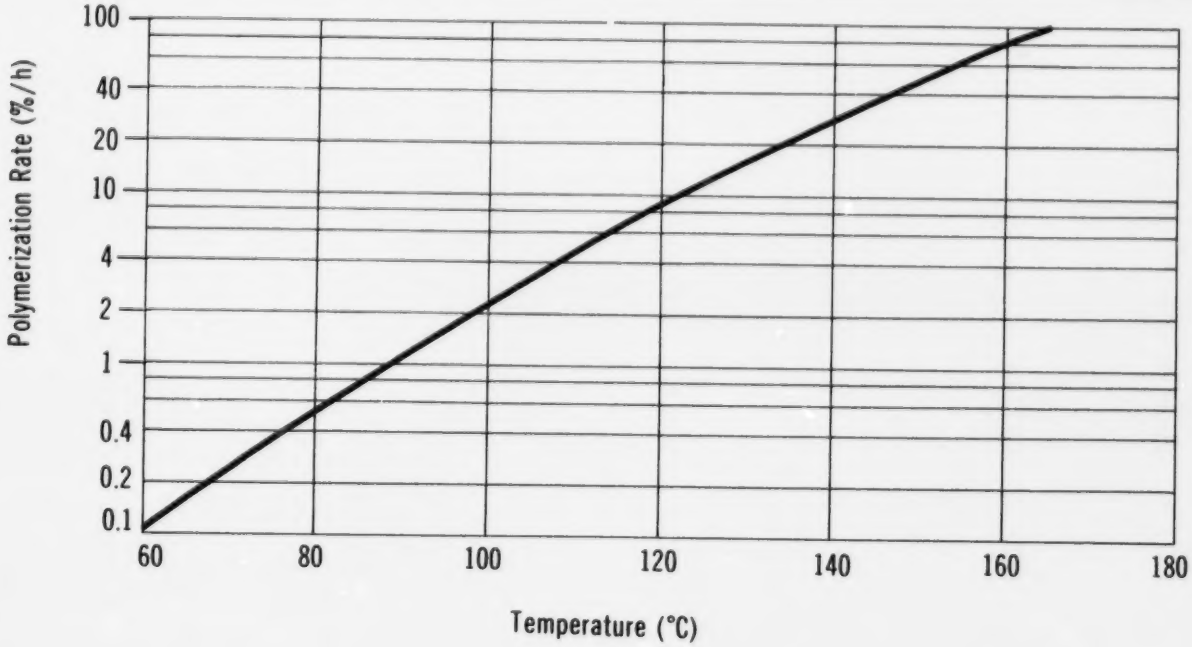


FIGURE 4

STYRENE

LIQUID VISCOSITY VS TEMPERATURE

Reference: Chem.Eng.1976

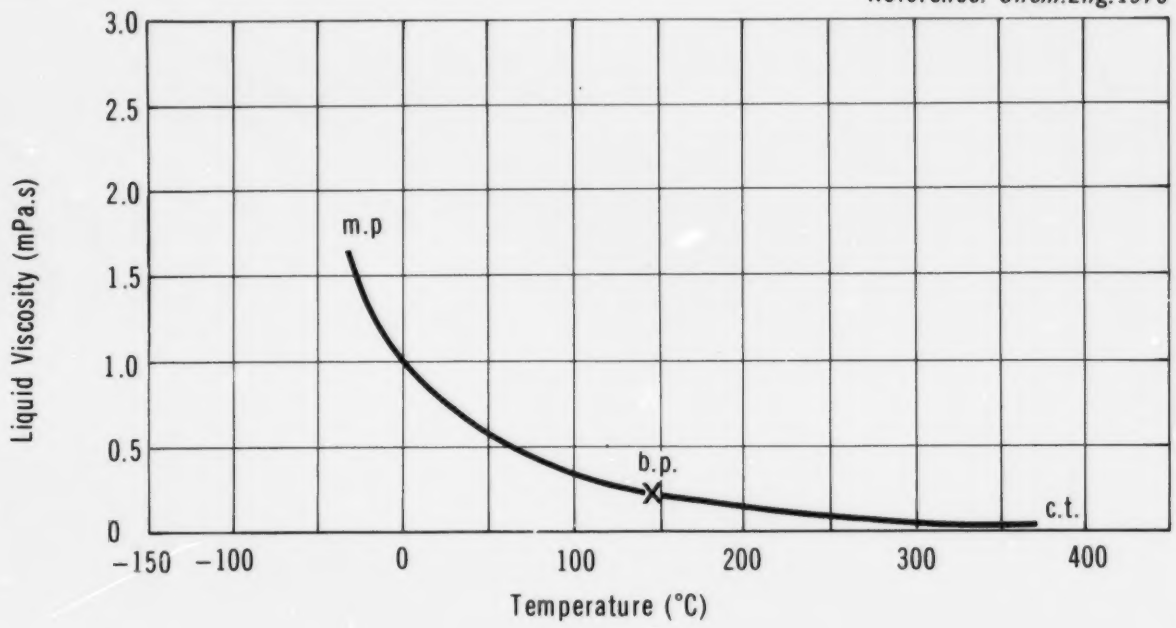


FIGURE 5

STYRENE

VAPOUR VISCOSITY VS TEMPERATURE

Reference: Chem.Eng. 1976

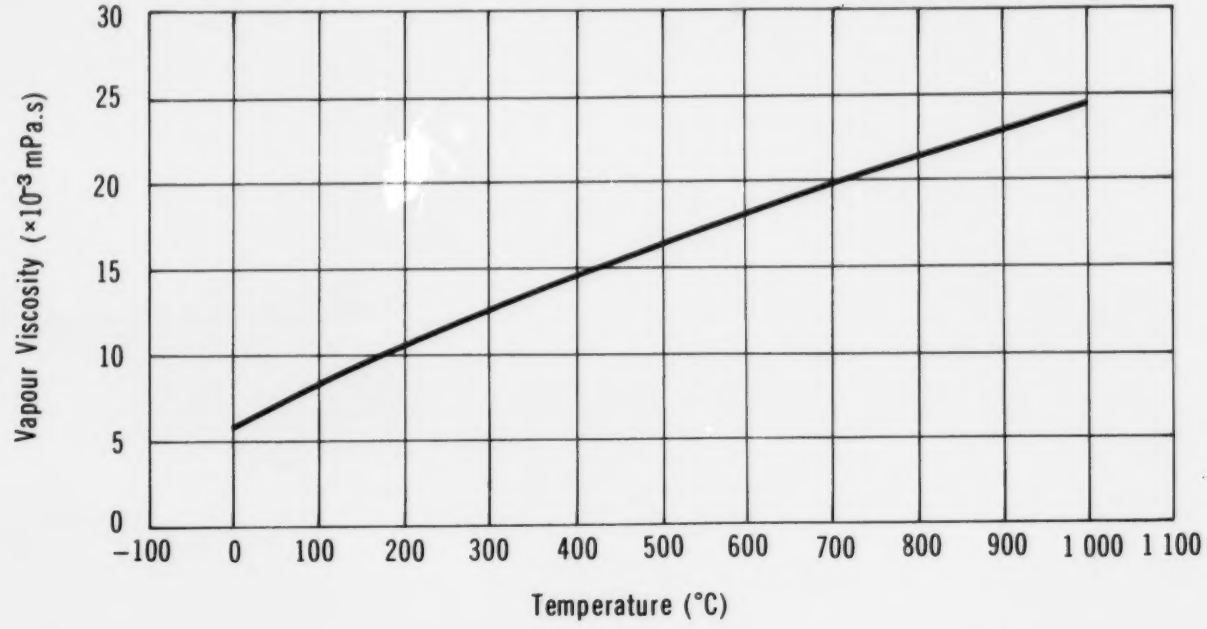
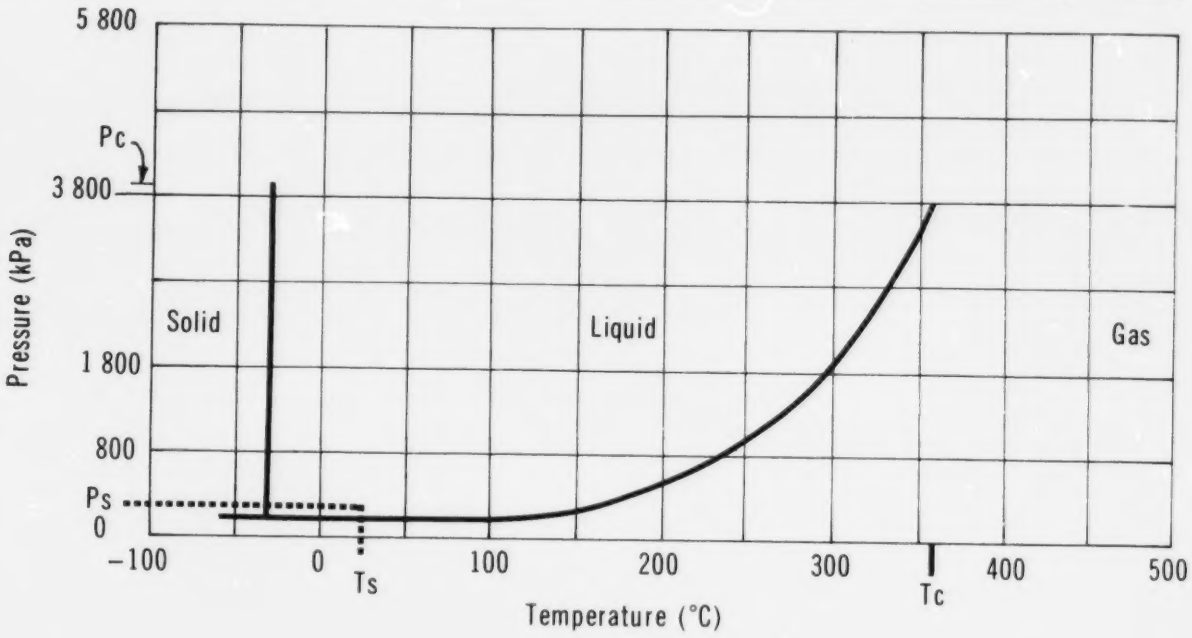


Figure 6

STYRENE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

Styrene is sold as a liquid with a purity of 99.5 or 99.6 percent with 10 to 60 ppm TBC (p-tert-butylcatechol) as an inhibitor. The contents of a typical commercial grade (polymerization grade) is as follows (Kirk-Othmer 1983; Brighton 1979; Santodonato 1980):

Styrene: 99.5-99.6 percent
Polymer: < 10 pm
TBC: 10-60 ppm
Ethylbenzene: 0.1 percent
Aldehydes: 70-200 ppm
Peroxides: 5-30 ppm
Chlorides: 5-10 ppm
Sulphur: 5-10 ppm
Water: 0.01 percent
Other C_8: 400-800 ppm
Other C_9: 500-1000 ppm

3.2 Domestic Manufacturers (Corpus 1983; CCPA 1981)

These are corporate headquarters' addresses and are not intended as spill response contacts.

Dow Chemical Canada Inc.
Box 1012
Modeland Road
Sarnia, Ontario
N7T 7K7
(519) 339-3131

Polysar Ltd.
201 Front Street North
Sarnia, Ontario
N7T 7V1
(519) 332-1212

3.3 Other Suppliers (CBG 1980; Scott 1979)

Apco Industries Co. Ltd.
10 Industrial Street
Toronto, Ontario
M4G 1Z1
(416) 421-6161

BASF Canada Ltd.
5850 Cote De Liesse
Montreal, Quebec
H4T 1C1
(514) 341-5411

Ciscohem Inc.
63 Selby Road
Brampton, Ontario
L6W 1K5
(416) 459-4540

CPS Chemical Canada Ltd.
6600 Trans-Canada Highway
Pointe Claire, Quebec
H9R 4S2
(514) 695-0610

International Chemical Canada Ltd.
P.O. Box 385
Brampton, Ontario
L6V 2L3
(416) 453-4234

Recochem Inc.
850 Montee De Liesse
Montreal, Quebec
H9S 1H7
(514) 341-3550

Pigment and Chemical Co. Ltd.
5757 Cavendish Blvd.
Montreal, Quebec
H4W 2W8
(514) 489-9396

3.4 Major Transportation Routes

Current Canadian production of styrene is all in the Sarnia area. Transportation of the product by tank cars or tank trucks occurs mainly in Ontario and Quebec, with a smaller amount to the western provinces.

3.5 Production Levels (Corpus 1983)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1981)
Dow Chemical Canada, Sarnia, Ont.		55
Polysar, Sarnia, Ont.		272
	TOTAL	327
Domestic Production (1982)		290.5
Imports (1982)		0.6
	TOTAL SUPPLY	291.1

3.6 Manufacture of Styrene (FKC 1975; Brighton 1979; Tossavainen 1978)

3.6.1 General. Ethylbenzene is catalytically dehydrogenated to form styrene.

3.6.2 Raw Materials. The raw material used in the manufacture of styrene is ethylbenzene.

3.6.3 Manufacturing Process. Purified ethylbenzene is preheated to 520°C, mixed with super-heated steam at 700°C and fed continuously to a reactor (at 600-650°C) containing a dehydrogenation catalyst (typically an oxide catalyst e.g., zinc or iron oxide). There the ethylbenzene is converted to styrene, at about 35 percent conversion per pass:

The reaction product passes to a series of heat exchanges to be cooled and condensed. Tars are condensed in the first heat exchanger; the final heat exchanger condenses steam, styrene, toluene and benzene; vent gases are sent to a refrigeration-recovery system.

The styrene-containing condensate has a polymerization inhibitor added and is vacuum-fractionated in a succession of columns. The polymerization inhibitor is again added to the styrene fraction, and it is sent to storage; ethylbenzene is recycled. The overall yield of styrene is about 90 percent.

3.7 Major Uses in Canada (Corpus 1983)

Styrene is used for production of polystyrene, ABS/SAN resins, SB lattices, SB rubbers, and polyester resins. In 1982, 44 percent of Canadian production was used for polystrene production and 36 percent was exported.

3.8 Major Buyers in Canada (Corpus 1983)

Alcore Fabricating, Richmond Hill, Ont.
Almatex, London, Ont.
Ashland Chemical, Mississauga, Ont.
Avmor, Montreal, Que.
BASF Canada, Laval, Que.
Borg-Warner Chemicals, Cobourg, Ont.
C-I-L Paints, Toronto, Ont.
Canadian General Electric, Toronto, Ont.
Du Pont Canada, Ajax, Ont.
Fiberglas Canada, Guelph, Ont.
Fiberplast Products, Winfield, B.C.
Glidden (SCM), Toronto, Ont.
ICL Engineering, Vancouver, B.C.
Inmont Canada, Toronto, Ont.
Iroquois Chemicals, Cornwall, Ont.
SC Johnson & Son, Brantford, Ont.
Mia Chemical, Toronto, Ont.
Monsanto Canada, LaSalle, Que.
Moore, Benjamin, Toronto, Ont.
Northwest Industries, Edmonton, Alta.
Polyresins, Toronto, Ont.
Potton Chemical, Mansonville, Que.
Precisioneering, Toronto, Ont.
Protective Plastics, Milliken, Ont.
Reichhold, Toronto, Ont.
Rohm & Haas, Toronto, Ont.
Schenectady Chemicals, Toronto, Ont.
Sherwin-Williams, Montreal, Que.
Temuss Products, Ajax, Ont.
Texstyrene Plastics, Baie d'Urfe, Que.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

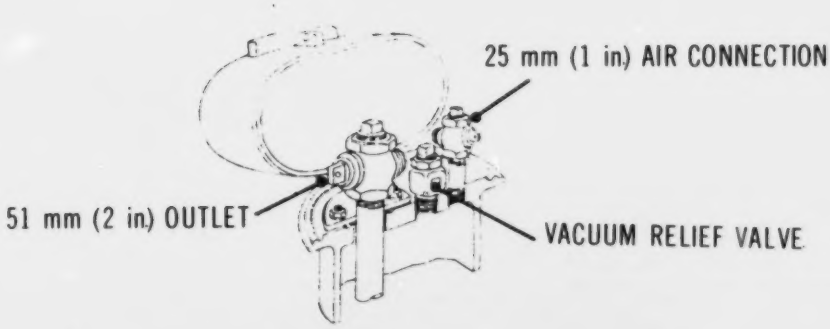
4.1.1 Bulk Shipment. Transportation vessels and containers under this category have been grouped under the classifications of railway tank cars and highway tank vehicles.

4.1.1.1 Railway tank cars. Railway tank cars used to transport styrene monomer are described in Table 2 (TCM 1979; RTDCR 1974). Figure 7 shows a CTC/DOT 111A60W1 railway car commonly used to transport styrene monomer; Table 3 indicates railway tank car details associated with this drawing. Cars are equipped for unloading by gravity flow through a 152 mm (6 in.) diameter bottom outlet provided with an inner plug valve (TDGC 1980). In addition to bottom unloading, the cars may be unloaded from the top by pump (MCA 1971). In this case, the liquid is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with an unloading connection valve. Air pressure is not recommended for unloading styrene monomer tanks; however, padding by nitrogen is recommended (CCPA 1983).

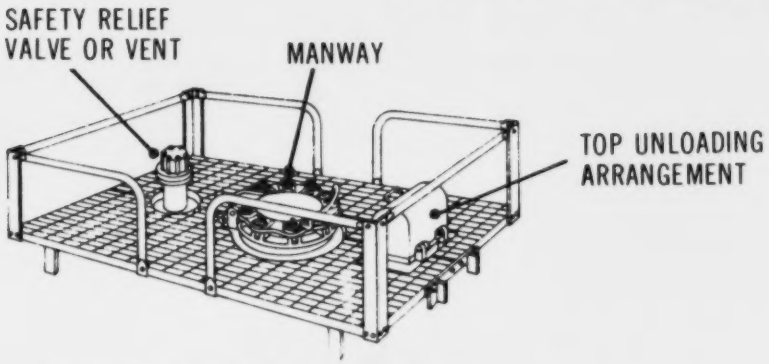
TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A60F1	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A100W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% miminum outage. Gauging device. Bottom outlet or washout optional. Test pressure 690 kPa (100 psi).
103W	Steel fusion-welded tank with dome. Uninsulated or insulated. 2% dome. Bottom outlet or washout optional
104W	Same as 103W but must be insulated.

* Canadian Transport Commission and Department of Transportation (U.S.)



Detail of top unloading arrangement



Detail of loading platform

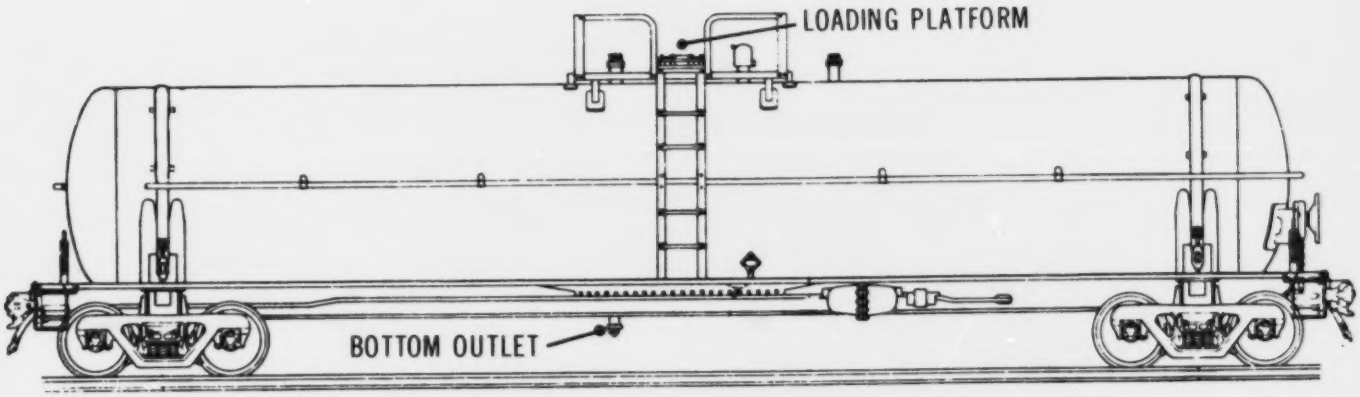


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 (TCM 1979; RTDCR 1974)

Description	Tank Car Size (Imp. Gal.) 16 700		17 200		20 000	
Overall						
Nominal capacity	75 700 L	(16 700 gal.)	78 000 L	(17 200 gal.)	90 900 L (20 000 gal.)	
Car weight - empty	33 900 kg	(74 700 lb.)	33 900 kg	(74 700 lb.)	38 900 kg (85 800 lb.)	
Car weight - (max.)	119 000 kg	(263 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg (263 000 lb.)	
Tank						
Material	Steel		Steel		Steel	
Thickness	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)
Inside diameter	2.60 m	(102 in.)	2.62 m	(103 in.)	2.74	(108 in.)
Test pressure	414 kPa	(60 psi)	414 kPa	(60 psi)	414 kPa	(60 psi)
Burst pressure	1640 kPa	(240 psi)	1640 kPa	(240 psi)	1640 kPa	(240 psi)
Approximate Dimensions						
Coupled length	17 m	(57 ft.)	17 m	(57 ft.)	18 m	(60 ft.)
Length over strikers	16 m	(53 ft.)	16 m	(53 ft.)	17 m	(57 ft.)
Length of truck centres	13 m	(42 ft.)	13 m	(42 ft.)	14 m	(45 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(13 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width (over grabs)	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2-3 m	(8-10 ft.)	2-3 m	(8-10 ft.)	2-3 m	(8-10 ft.)
Width of grating	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)
Loading/Unloading Fixtures						
Top Unloading						
Unloading connection	51 mm	(2 in.)	51 mm	(2 in.)	51 mm	(2 in.)
Manway/fill hole	203-356 mm	(8-14 in.)	203-356 mm	(8-14 in.)	203-356 mm	(8-14 in.)
Air connection	25-51 mm	(1-2 in.)	25-51 mm	(1-2 in.)	25-51 mm	(1-2 in.)
Bottom Unloading						
Bottom outlet	102-152 mm	(4-6 in.)	102-152 mm	(4-6 in.)	102-152 mm	(4-6 in.)
Safety Devices	Safety vent or valve					
Dome	None					
Insulation	Optional					

A safety vent set at 414 kPa (60 psi) is required on top of the rail car. A gauging device, either the rod type or the tape type, should be used. The top unloading connection must be protected by a housing. The maximum pressure allowable for the 111A100W1 rail cars is 448 kPa (65 psi). When the 111A60W1 or 111A60F1 cars are used, this maximum pressure would be 276 kPa (40 psi) (TCM 1979).

4.1.1.2 Tank motor vehicles. Styrene monomer is transported by tank motor vehicles with tanks classed as nonpressure vessels. Design pressure for such tanks must not exceed 101 kPa (15 psi). Motor vehicle tanks are similar to the railway tanks previously described. These highway tankers are usually unloaded by pump from the top unloading connection valve (MCA 1971).

The off-loading equipment and procedures for tank motor vehicles are similar to those for railway tank cars, to be discussed later.

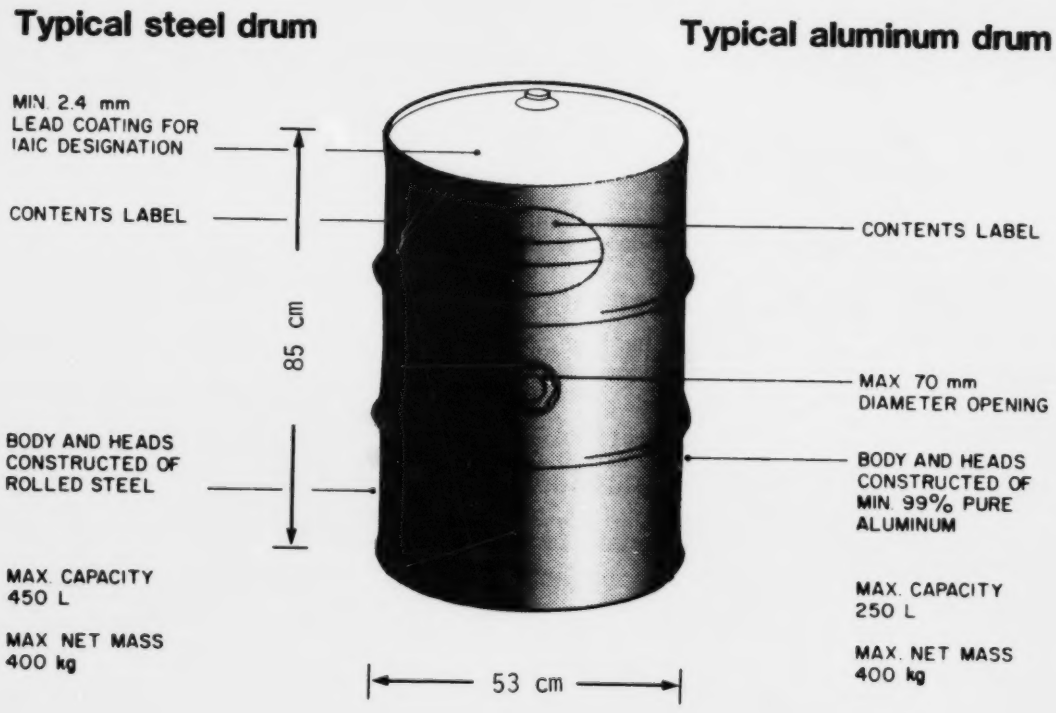
4.1.2 Packaging. Styrene monomer is also occasionally transported in drums. Drums fabricated from a variety of construction materials are permitted (TDGC 1980). The most commonly used drums are lined and unlined blank iron, stainless steel, and aluminum (Table 4) (CCPA 1983).

TABLE 4 DRUMS

Type of Drum	Designation	Description	Figure No. (If any)
Steel	1A1	Nonremovable head, reusable	8
	1A1A	1A1 with reinforced chime	8
	1A1B	1A1 with welded closure flange	8
	1A1D	1A1 with coating (other than lead)	8
	1A2	Removable head, reusable	8
	1A3	Nonremovable head, single use only	8
Aluminum	1B1	Nonremovable head	8
	1B2	Removable head	8
Steel Drums with inner plastic receptacles	6HA1	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.)	
Fibreboard Drums with inner plastic receptacles	6HG1	Outer containers of convolutely wound plies of fibreboard. Inner plastic in shape of drum. Maximum capacity of 225 L (49 gal.)	

FIGURE 8

TYPICAL DRUM CONTAINERS


Typical steel drum
Typical aluminum drum
MIN. 2.4 mm LEAD COATING FOR IAIC DESIGNATION
CONTENTS LABEL
85 cm
BODY AND HEADS CONSTRUCTED OF ROLLED STEEL
MAX. CAPACITY 450 L
MAX. NET MASS 400 kg
CONTENTS LABEL
MAX. 70 mm DIAMETER OPENING
BODY AND HEADS CONSTRUCTED OF MIN. 99% PURE ALUMINUM
MAX. CAPACITY 250 L
MAX. NET MASS 400 kg
53 cm

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1971):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution signs displayed.
- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Effectively ground the tank car.

Two means of off-loading are used for styrene rail cars, top off-loading and bottom off-loading (MCA 1971).

Proceed with top off-loading as follows:

- Relieve tank of internal vapour pressure by cooling tank with water or venting tank at short intervals.
- After removing the protective housing from the discharge line at the top of the car, connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pump only or pad the car with nitrogen to prime the pump and keep a slight positive pressure on the car during the unloading process (CCPA 1983).

Proceed with bottom off-loading in the following manner using gravity flow:

- Relieve internal pressure as previously mentioned.
- After connecting the unloading line to a 152 mm (6 in.) bottom outlet, open the inside bottom valve by turning the valve rod handle at the top of the car.
- Off-load the car by gravity.
- The car should be vented during the off-loading process to keep it from pulling a vacuum on itself even if equipped with a vacuum release valve (CCPA 1983).

4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in styrene monomer service. It is recognized that other materials may be used for particular applications, as indicated in Table 5. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets and pumps.

Iron and galvanized steel pipe are the most commonly used materials (CCPA 1983). Schedule 40 seamless ASTM A106 carbon steel pipes and fittings lined with polyvinylidene chloride (Saran) resins are recommended for styrene monomer lines (Dow PPS 1972). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak after a very short time. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipeline should be tested with air at pressures from 345 to 518 kPa (50-75 psi) and all leaks carefully stopped. If leaks develop in service, the only satisfactory way to repair them is to chip out the bad weld and reweld, or replace the section of pipe.

The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on liquid tank cars; however, process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining.

Jointed unloading arms of aluminum may be used with packing of Viton. Flexible metal (woven) or Viton elastomer hoses may also be used. (CCPA 1983). Flexible

bellows-type expansion joints can be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion members molded from tetrafluoroethylene resin (Dow PPS 1972). Some installations of flexible line are made with standard lined fittings using a number of flanged elbows. "Bacco chicksen" joints are also frequently employed (CCPA 1983).

Cast iron or cast steel diaphragm valves lined with polyvinylidene chloride resin will serve adequately (DPLV 1972). Viton may be used as a gasket material at normal temperature ranges. Transfer lines and joints should be emptied to avoid contact of styrene with synthetic gaskets and seals.

The use of double-seal centrifugal pumps is recommended over sealless pumps (CCPA 1983). A single-suction, sealless magnetic drive centrifugal pump with "wet end" material of 316 stainless steel may also be used. Leakage from this type of pump is virtually eliminated. Provision must be made for draining the pump so that repairs can be made safely (MCA 1971). The pump should be equipped with flanges at both suction and discharge openings; screw connections are more subject to leakage and should be avoided.

4.3 Compatibility with Materials of Construction

The compatibility of styrene monomer with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings		24	PVDC (DCRG 1978) FPM Hose (MCA 1971) Viton hose Steel Stainless steel (Dow 1981)		Copper Copper Alloys (Brighton 1979) NR Hose (MCA 1971)

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
2. Pumps	100%	38	GRP with FPM A "0" ring		
3. Storage Tanks			CS Black Iron Galvanized Iron		Copper Copper Alloy
4. Others			Iron, Steel, Magnesium Alloys (Brighton 1979)		NR, SBR, CR, NBR, IIR, CSM, EPDM (GPP)
	100%	24-100	Glass (CDS 1967)		

TABLE 6 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
	Aluminum
CR	Polychloroprene (Neoprene) Rubber
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
GRP	Glass Reinforced Vinyl Ester
	Iron, Galvanized
	Iron, Black
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel-Copper Alloy (Monel)
PVDC	Polyvinylidene Chloride
	Steel
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
	Stainless Steel

5 CONTAMINANT TRANSPORT

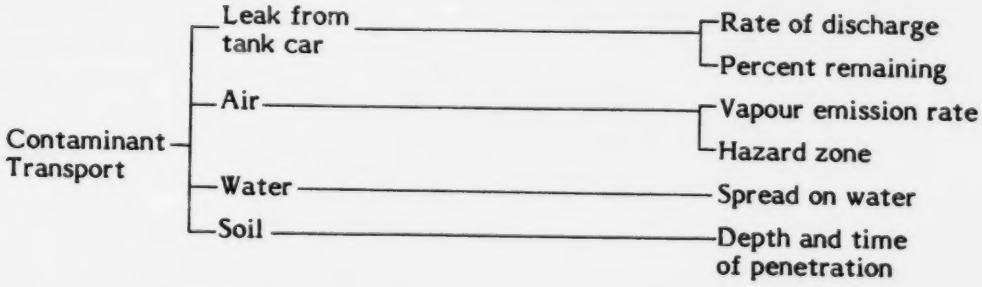
5.1 General Summary

Styrene is a moderately volatile liquid that is commonly transported in railway tank cars. When spilled in the environment, it will form a liquid pool, spreading on the surface of a water body or on the ground, being adsorbed onto the soil. The irritating flammable vapour is released continuously to the atmosphere by evaporation.

When spilled on water, the slick has a natural tendency to spread. Since it is only slightly soluble and less dense than water, only a very small amount will be dissolved in the water, the rest evaporating to the atmosphere.

Styrene, when spilled on the ground, is gradually adsorbed onto the soil, at a rate dependent on the soil type and its degree of saturation with water. At the same time, the downward transport of the liquid toward the groundwater table may be an environmental problem.

The following factors are considered for the transport of a styrene spill in the air, water and soil media:



It is important to note that because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Styrene is commonly transported in railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size

has been chosen throughout the EnviroTIPS series for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with styrene is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the moderate volatility of styrene and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

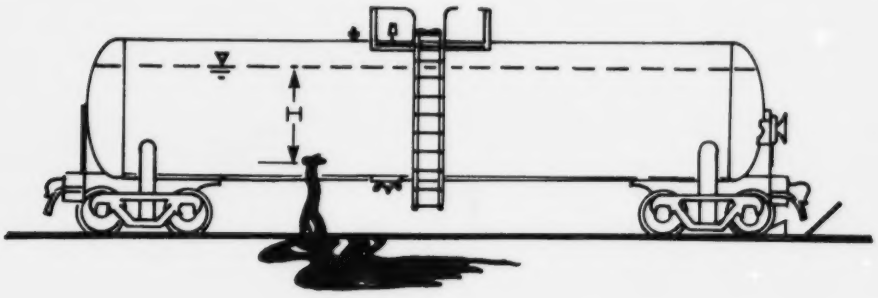


FIGURE 9 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

5.2.2 Nomograms.

5.2.2.1 Figure 10: Percent remaining versus time. Figure 10 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of styrene. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

5.2.2.2 Figure 11: Discharge rate versus time. Figure 11 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture, for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

FIGURE 10

STYRENE

PERCENT REMAINING VS TIME

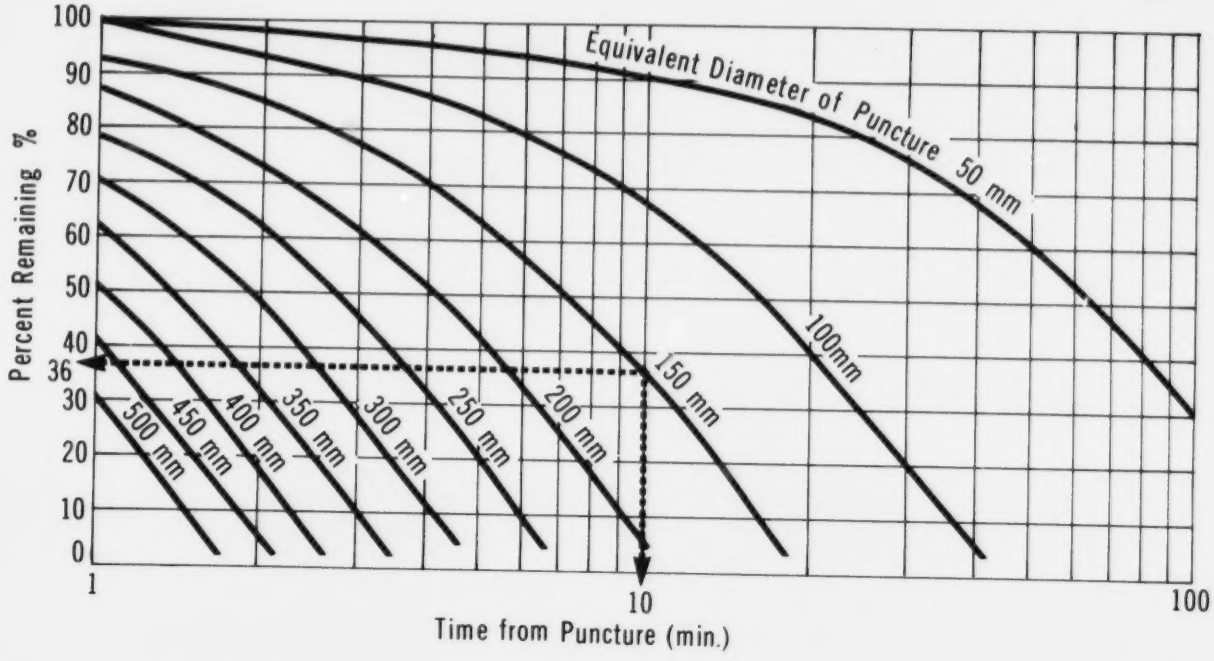
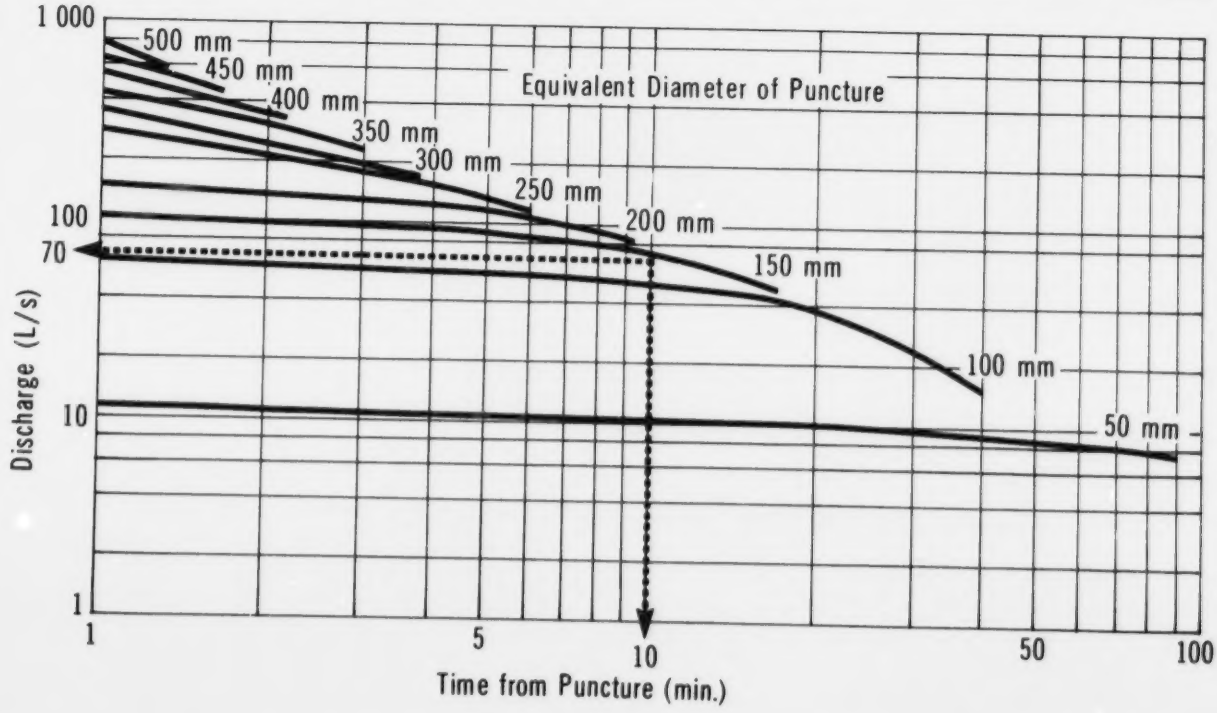


FIGURE 11

STYRENE

DISCHARGE RATE VS TIME



5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with styrene has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 10
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- Use Figure 11
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since styrene is a moderately volatile liquid, direct venting of the vapour to the atmosphere from a hole in punctured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground or water surface is treated here.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

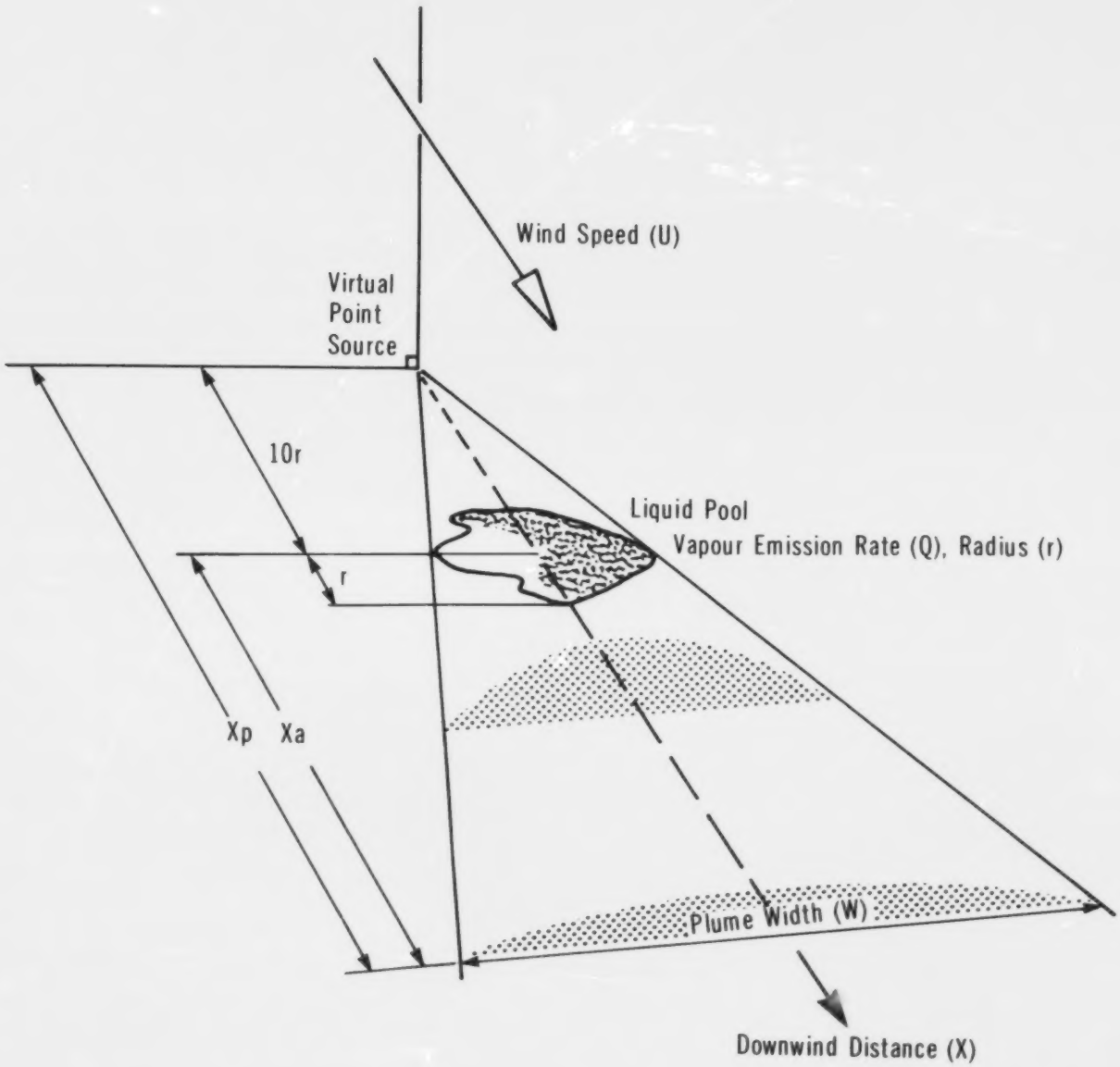
Figure 12 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source as a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud.

FIGURE 12

STYRENE

SCHEMATIC OF CONTAMINANT PLUME



The following nomograms and data tables are contained in this section (to be used in order given):

Figure 14:	vapour emission rate from a liquid pool as a function of maximum pool radius
Table 7:	weather conditions
Figure 15:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 8:	maximum plume hazard half-widths
Figure 18:	vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flow chart given in Figure 13 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" and "equivalent pool radius" are contained in Sections 5.2 and 5.4, respectively. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 14: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for styrene has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for styrene at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.13 g/(m^2s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation which at a given wind speed is dependent on ambient temperature and the vapour pressure (Chem. Eng. 1976) of styrene at that temperature. For example, evaporation rates of 0.033 g/(m^2s) at 0°C and 0.26 g/(m^2s) at 30°C were calculated for a wind speed of 4.5 m/s.

Using Figure 21, Section 5.4, the maximum spill radius corresponding to various spill amounts of styrene may be determined. The resultant spill areas and the styrene evaporation rates provide the basis for preparation of the vapour release rate versus spill radius nomogram in Figure 14.

Use: For a pool of styrene of known radius, the rate (Q) at which styrene vapour is released to the atmosphere at a given temperature can then be estimated from Figure 14. The solid portions of the curves represent spills of 0.1 to 72.5 tonnes, the latter representing about one standard 80 000 L rail car load of styrene. It should be noted that Figure 14 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of styrene vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the

FIGURE 13

STYRENE

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE

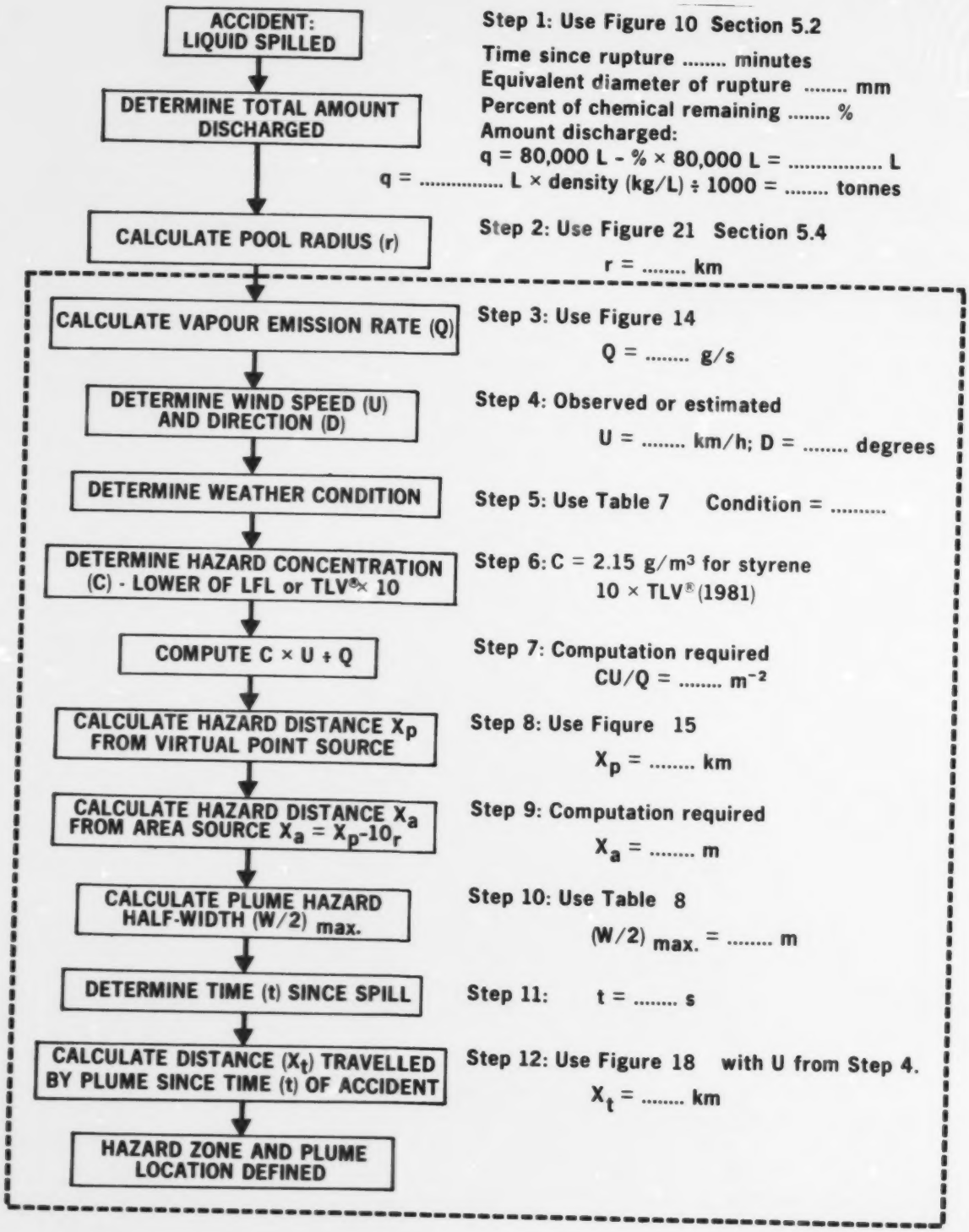
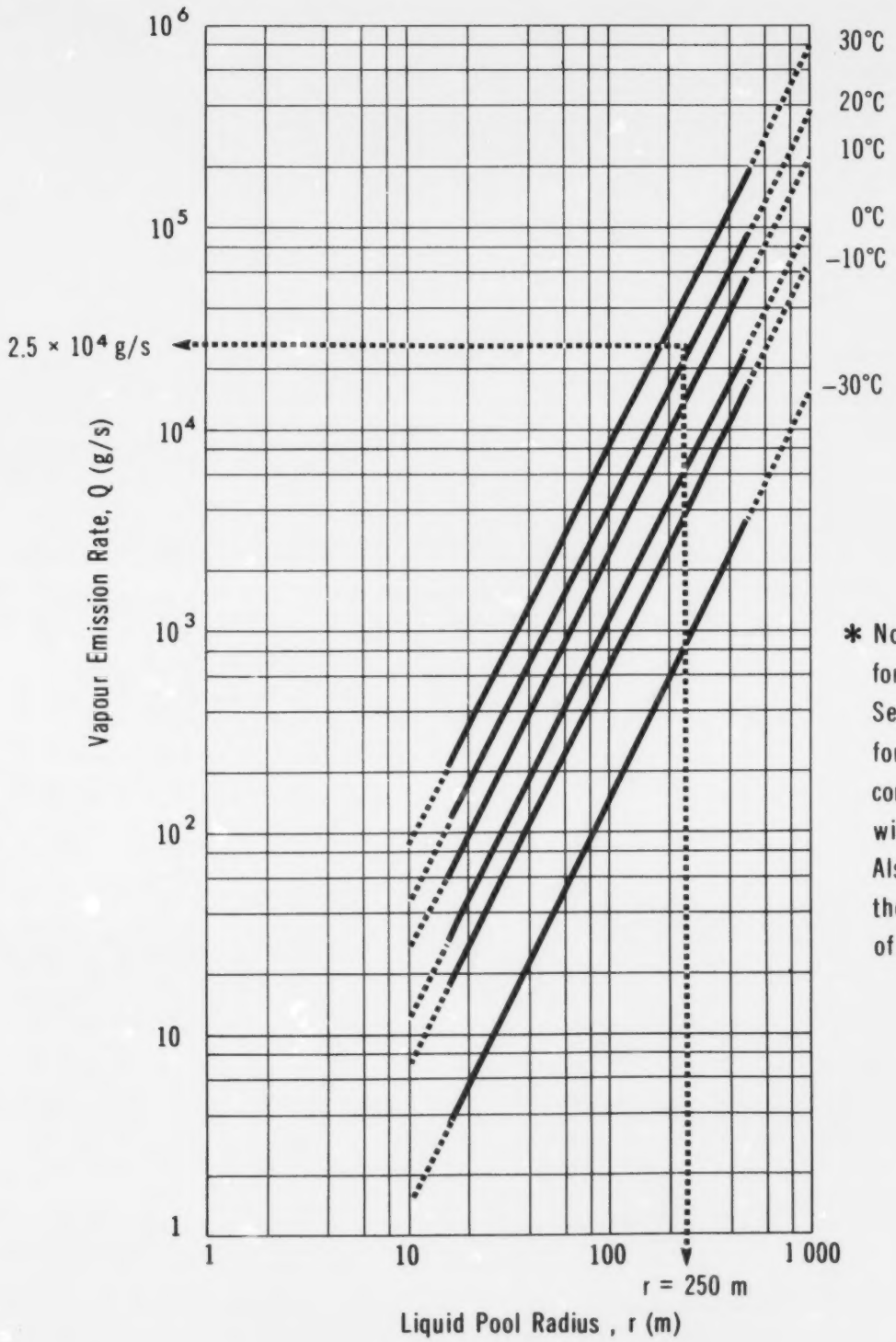

ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
CALCULATE POOL RADIUS (r)
CALCULATE VAPOUR EMISSION RATE (Q)
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV® × 10
COMPUTE C × U ÷ Q
CALCULATE HAZARD DISTANCE Xp FROM VIRTUAL POINT SOURCE
CALCULATE HAZARD DISTANCE Xa FROM AREA SOURCE Xa = Xp-10r
CALCULATE PLUME HAZARD HALF-WIDTH (W/2) max.
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (Xt) TRAVELLED BY PLUME SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PLUME LOCATION DEFINED
Step 1: Use Figure 10 Section 5.2
Time since rupture ..... minutes
Equivalent diameter of rupture ..... mm
Percent of chemical remaining ..... %
Amount discharged:
q = 80,000 L - % × 80,000 L = ... L
q = ... L × density (kg/L) ÷ 1000 = ... tonnes
Step 2: Use Figure 21 Section 5.4
r = ... km
Step 3: Use Figure 14
Q = ... g/s
Step 4: Observed or estimated
U = ... km/h; D = ... degrees
Step 5: Use Table 7 Condition = ...
Step 6: C = 2.15 g/m3 for styrene
10 × TLV® (1981)
Step 7: Computation required
CU/Q = ... m-2
Step 8: Use Fiqure 15
Xp = ... km
Step 9: Computation required
Xa = ... m
Step 10: Use Table 8
(W/2) max. = ... m
Step 11: t = ... s
Step 12: Use Figure 18 with U from Step 4.
Xt = ... km

FIGURE 14

STYRENE

VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



* Note: Nomogram applies for wind speed of 4.5 m/s See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.1 to 72 .5 tonnes.

evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

It should also be noted that the determination of the emission rate is based on the spill radius on calm water (Table T1, CHRIS 1974). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to provide the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius would be overestimated and worst case values are provided.

5.3.2.2 Figure 15: Vapour concentration versus downwind distance. Figure 15 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 15, the weather condition must be determined from Table 7.

TABLE 7 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed < 11 km/h (≃ 3 m/s) and one of the following:	Most other weather conditions
- overcast day	
- night time	
- severe temperature inversion	

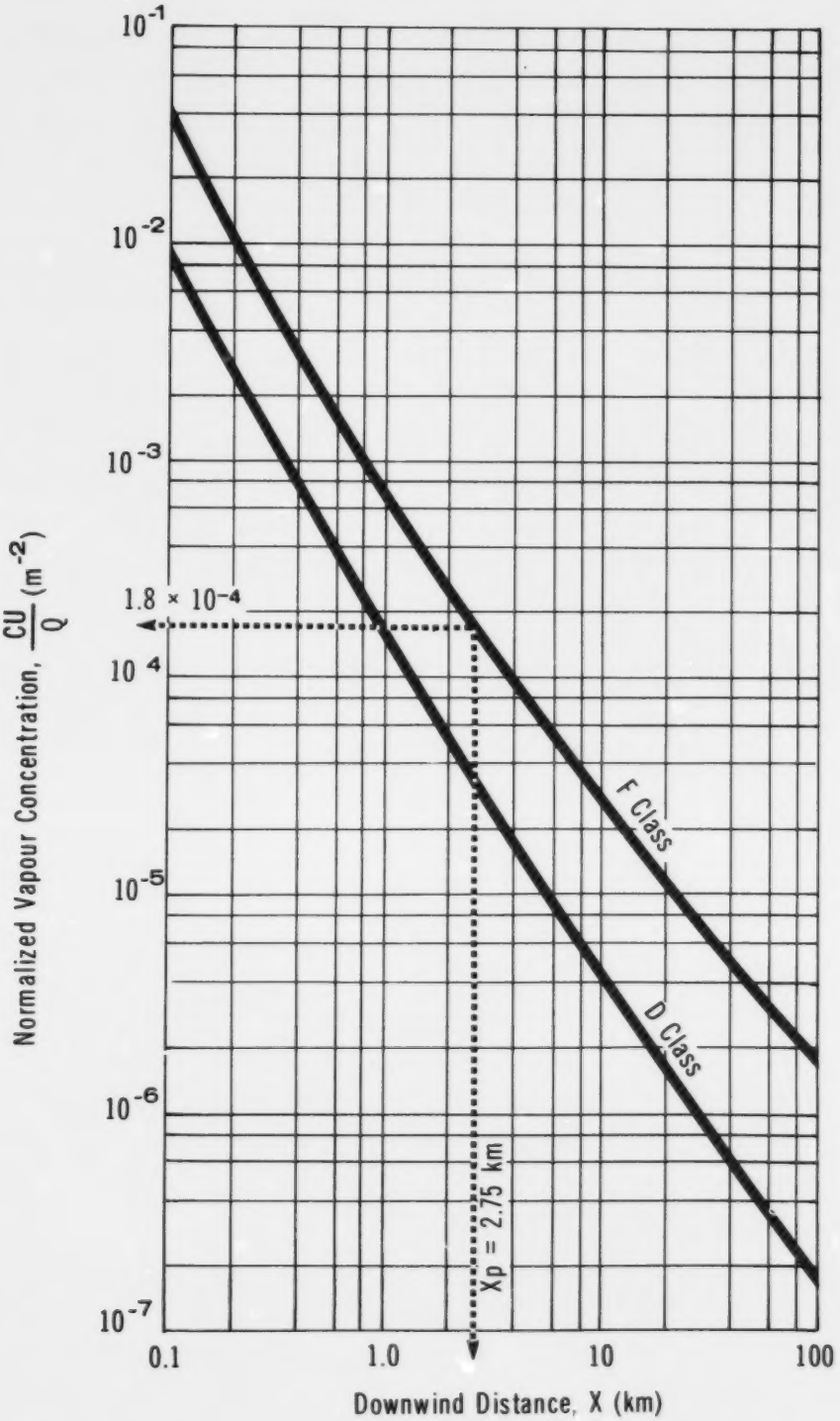
Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 15 knowing:

- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value® (TLV, in g/m^3), or the Lower Flammability Limit (LFL, in

FIGURE 15

STYRENE

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



g/m^3). Note: To convert the TLV® (in ppm) and the LFL (in percent by volume) to concentrations in g/m^3, use Figures 16 and 17

A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.3 Table 8: Maximum plume hazard half-widths. This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the styrene Threshold Limit Value (TLV®) of 0.215 g/m^3, or 2.15 g/m^3. The maximum plume hazard half-width represents the maximum half-width of the styrene vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 8 is therefore only applicable for a styrene hazard concentration limit of 10 x TLV®, or 2.15 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 30 000 to 15 000 000 g/s, corresponding to styrene spills in the range of about 25 to 7500 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 72 500 kg, or approximately 73 tonnes. Therefore, under Class D of Table 8, data are provided for up to 100 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 3000 to 1 250 000 g/s, corresponding to styrene spills in the range of about 2 to 1000 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 13 times a standard rail car load.

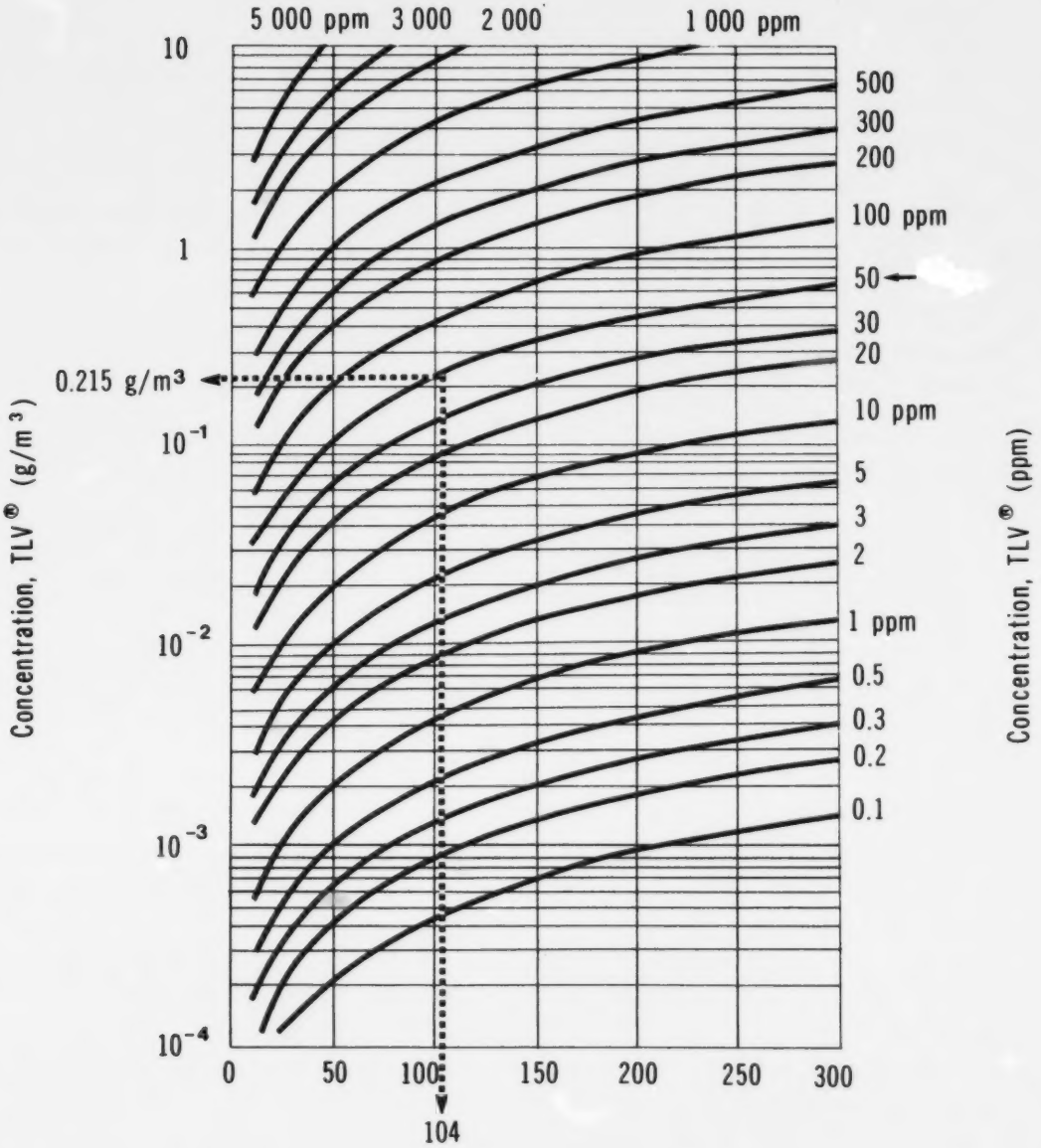
Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{max}$, the maximum plume hazard half-width, in metres. (For an intermediate value, interpolate Q/U and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 8.

5.3.2.4 Figure 18: Plume travel time versus travel distance. Figure 18 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

FIGURE 16

STYRENE

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



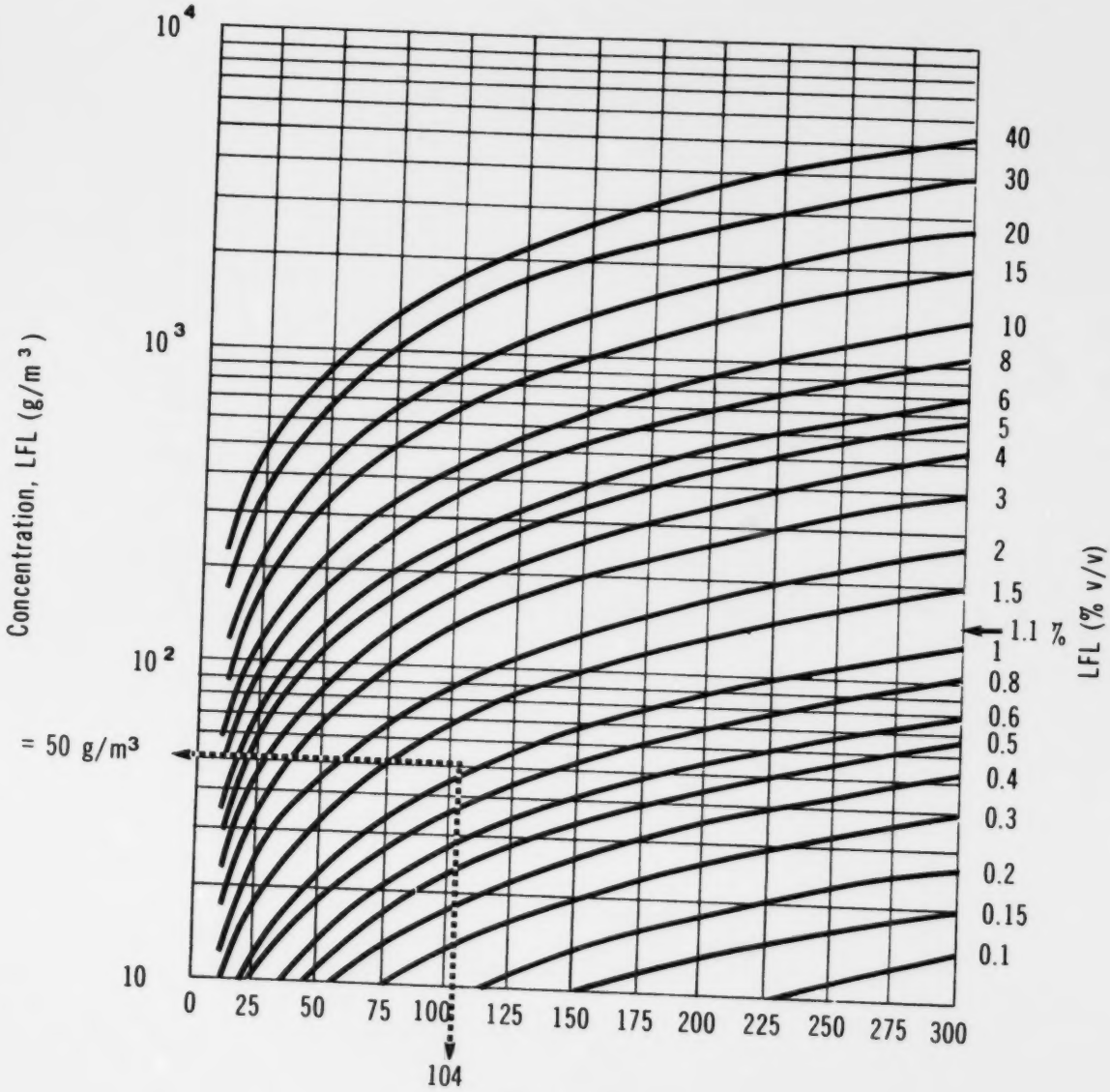
Example: Styrene, MW = 104, TLV® = 50 ppm,
then TLV® in g/m³ = 0.215

Note: data applicable at 25° and 760 mm Hg pressure

STYRENE

FIGURE 17

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example : Styrene, MW = 104, LFL = 1.1%, then LFL in g/m³ = 50

Note: data applicable at 25°C and 760 mm Hg pressure

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (for styrene at 20°C)

Weather Condition D			Weather Condition F		
Q/U (g/m)	$(W/2)_{max}$ (m)		Q/U (g/m)	$(W/2)_{max}$ (m)	
15 000 000	3420	(99.5 km)*	1 250 000	1400	(97.4 km)*
12 500 000	3060		1 000 000	1180	
10 000 000	2660		750 000	955	
7 500 000	2230		500 000	705	
5 000 000	1730		250 000	420	
2 500 000	1130		200 000	355	
2 000 000	980		150 000	295	
1 500 000	820		100 000	230	
1 000 000	640		75 000	190	
750 000	545		50 000	145	
500 000	430		25 000	95	
250 000	285	Q/U = 11 900 →	10 000	55	→ $(W/2)_{max}$ = 60 m
200 000	250		7 500	45	
150 000	210		5 000	35	
100 000	165		2 500	25	
75 000	140		1 000	15	
50 000	110				
25 000	75				
10 000	45		* Data are provided up to a maximum downwind hazard distance of 100 km.		
5 000	30				
2 500	20				
1 000	15				

Example: A spill releasing styrene vapour at the rate of Q = 2.5 x 10^4 g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 11 900 g/m which results in a maximum plume hazard half-width $(W/2)_{max}$ = 60 m.

Note: Above table is valid only for a styrene concentration of 10 x TLV®, or 2.15 g/m^3.

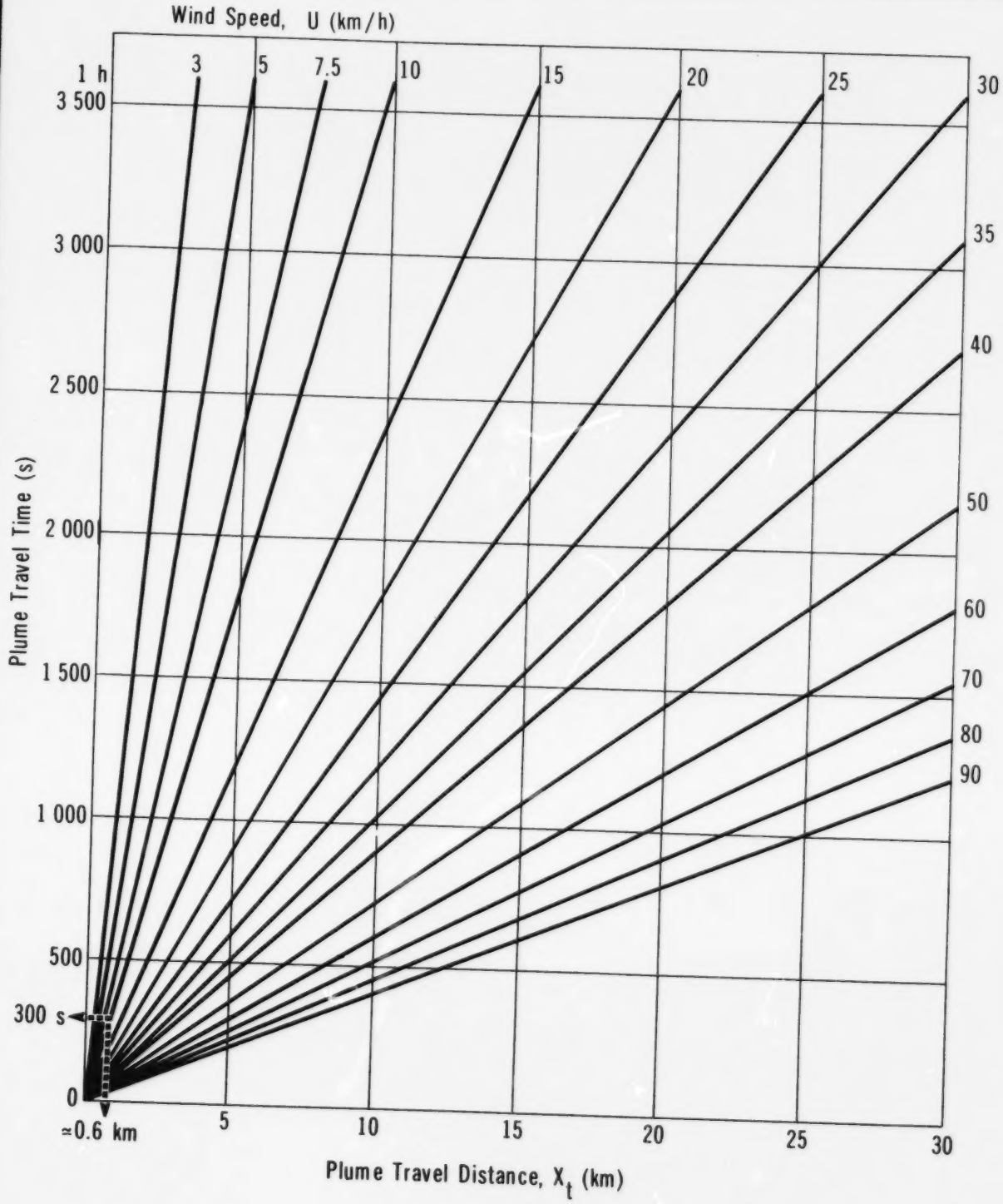
Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the plume has travelled.

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid styrene. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill radius) in a particular spill situation if possible.

STYRENE

FIGURE 18

PLUME TRAVEL TIME VS TRAVEL DISTANCE



Problem:

During the night, at about 2:00 a.m., 20 tonnes of styrene were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution:

Step 1: Quantity spilled is given, q = 20 tonnes

Step 2: Determine the pool radius (r) for a spill of 20 tonnes

- Use observed (measured) pool radius if possible. If not, use the maximum radius from Figure 21, Section 5.4. Note that use of these data, which apply specifically to spills on water, will result in an exaggerated pool radius on land
- Radius (r) = 250 m ÷ 1000 = 0.25 km

Step 3: Calculate the vapour emission rate (Q) at T = 20°C

- From Figure 14, for r = 250 m and T = 20°C, $Q = 2.5 \times 10^4$ g/s

Step 4: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given:

  U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s

  D = NW or 315°C (D = Direction from which wind is blowing)

Step 5: Determine the weather condition

- From Table 7, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine the hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL, so for styrene

  $C = 2.15$ g/m^3 (TLV® = 0.215 g/m^3; LFL = 50 g/m^3)

Step 7: Compute CU/Q

- $CU/Q = \dfrac{2.15 \times 2.1}{2.5 \times 10^4} = 1.81 \times 10^{-4}$ m^{-2}

Step 8: Calculate the downwind distance (X_p) from the virtual point source

- From Figure 15, with $CU/Q = 1.81 \times 10^{-4}$ m^{-2} and weather condition F, $X_p \simeq 2.75$ m

Step 9: Calculate the hazard distance (X_a) downwind of the area source

- With $X_p = 2.75$ km and r = 0.25 km then

  $X_a = X_p - 10r = 2.75$ km $- 10$ (0.25 km) $= 0.25$ km

Step 10: Calculate the plume hazard half-width $(W/2)_{max}$

- Use Table 8
- with $Q = 2.5 \times 10^4$ g/s and U = 2.1 m/s
  then $Q/U = \frac{2.5 \times 10^4}{2.1} = 11\,900$ g/m
- Then for weather condition, F the closest Q/U value is between 10 000 and 25 000 g/m, which gives $(W/2)_{max} \simeq 60$ m

Step 11: Determine the time since the spill

- t = 5 min x 60 = 300 s

Step 12: Calculate the distance travelled (X_t) by the vapour plume since the time of the accident

- Using Figure 18, with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 13: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (60 m) by the maximum hazard distance downwind of the area source (0.25 km) along the direction of the wind, as shown in Figure 19
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° $\pm$ 10°), the hazard zone is defined as shown in Figure 20
- Note that for a wind speed of 7.5 km/h the styrene vapour plume will have travelled 0.63 km in the 5 min since the spill occurred and that the downwind hazard distance is only 0.25 km

5.4 Behaviour in Water

5.4.1 Introduction. The rate of spreading on water is based on the balance between forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces).

In addition to the natural spreading tendency, the spill slick will move in the same direction and at the same speed as the surface water. Surface water direction and speed are influenced by currents and wind forces.

FIGURE 19

STYRENE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

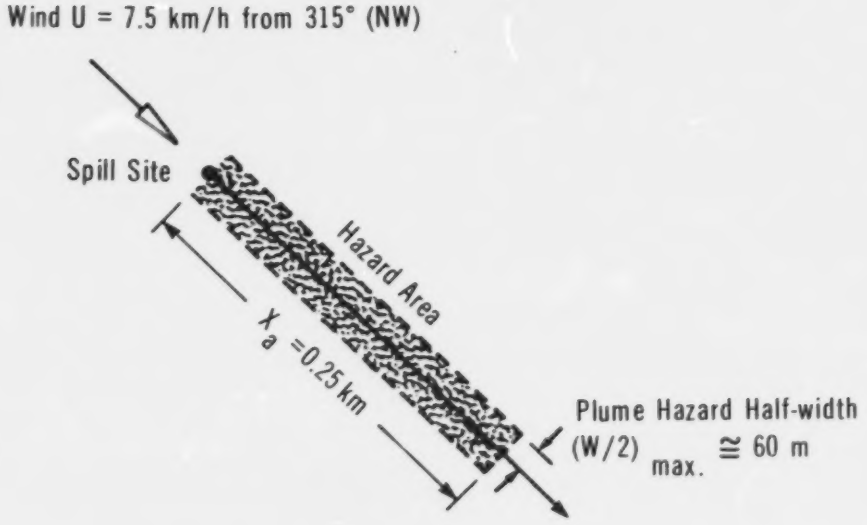
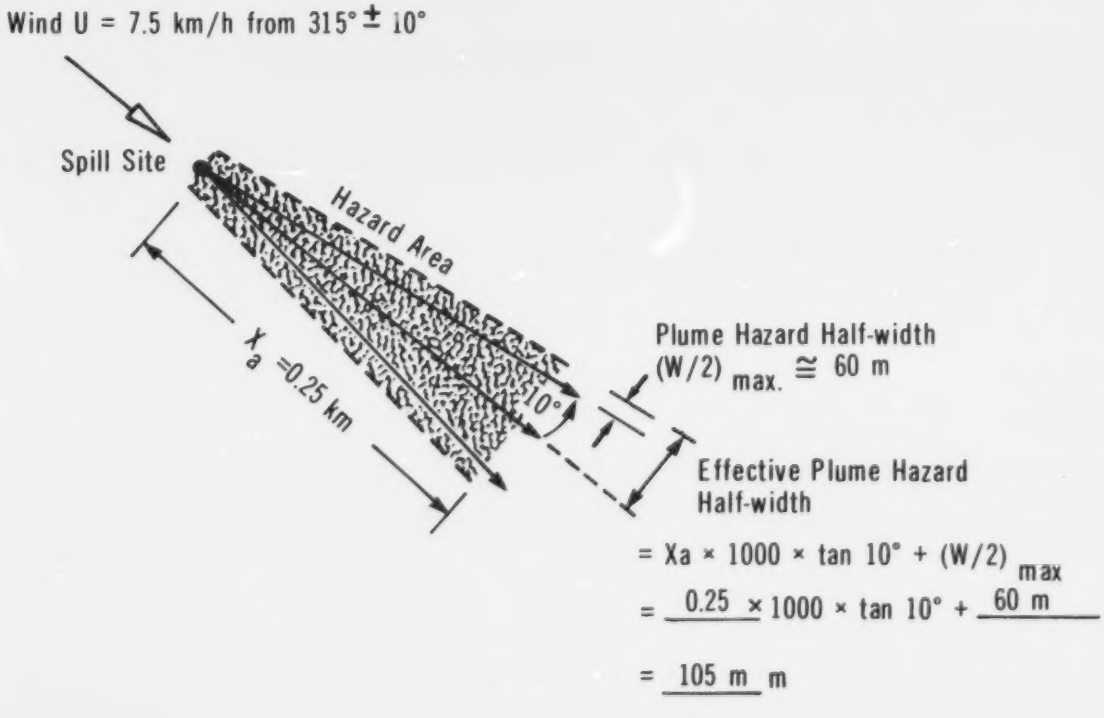


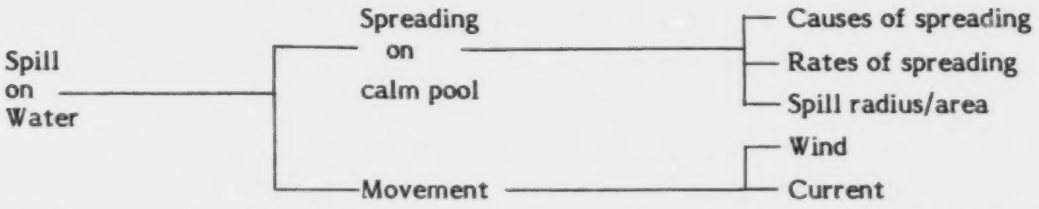
FIGURE 20

STYRENE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
X_a = 0.25 km
10°
Plume Hazard Half-width
$(W/2)_{max.} \cong$ 60 m
Effective Plume Hazard Half-width
= Xa × 1000 × tan 10° + $(W/2)_{max}$
= 0.25 × 1000 × tan 10° + 60 m
= 105 m m

Factors considered in the spill nomograms are illustrated in the following chart:



5.4.2 Nomograms. The following nomograms are presented to simplify calculations:

Figure 21: spill radius versus time (still water - unconfined) for various sizes of spills; maximum spill radius indicated

Figure 22: length of channel affected versus equivalent spill radius (still water - confined) for a number of stream widths

Figure 23: translation distance versus time for a range of surface water velocities

Figure 24: vectoral addition of surface current and wind

5.4.2.1 Figure 21: Spill radius versus time (still water - unconfined). Figure 21 provides a means of calculating the radius/area of an unconfined slick of styrene for a known mass of spill and at a defined time from the occurrence of the spill. The equations representing the spreading of the spill on water are presented in the Introduction Manual. A critique of the spreading model (Eisenberg 1975) suggests that the equations are valid for cases where the viscosity of the spilled liquid is greater than or equal to 0.2 times the viscosity of water ($U_L \geq 0.2\ U_W$).

For the purposes of the nomogram presented, the water/spill temperature has been taken at 20°C, representing a reasonable maximum for surface water bodies. This condition maximizes the spill size at any time of interest. If the indicated pool radius is larger than the theoretical maximum radius, use the theoretical maximum pool radius.

5.4.2.2 Figure 22: Length of channel affected versus equivalent spill radius (still water - confined). If the distance between the banks of the water body is less than the spill diameter, the slick will be confined. Using the effective radius of spill from Figure 21, the approximate length of channel affected by the spill can be computed from Figure 22, if the stream width is known.

5.4.2.3 Figure 23: Translation distance versus time (no wind). Figure 23 presents a simple relationship between velocity, time, and distance. The distance a spill will be translated in time by a flowing stream is directly proportional to the surface current.

FIGURE 21

STYRENE

SPILL RADIUS VS TIME
(still water - unconfined)

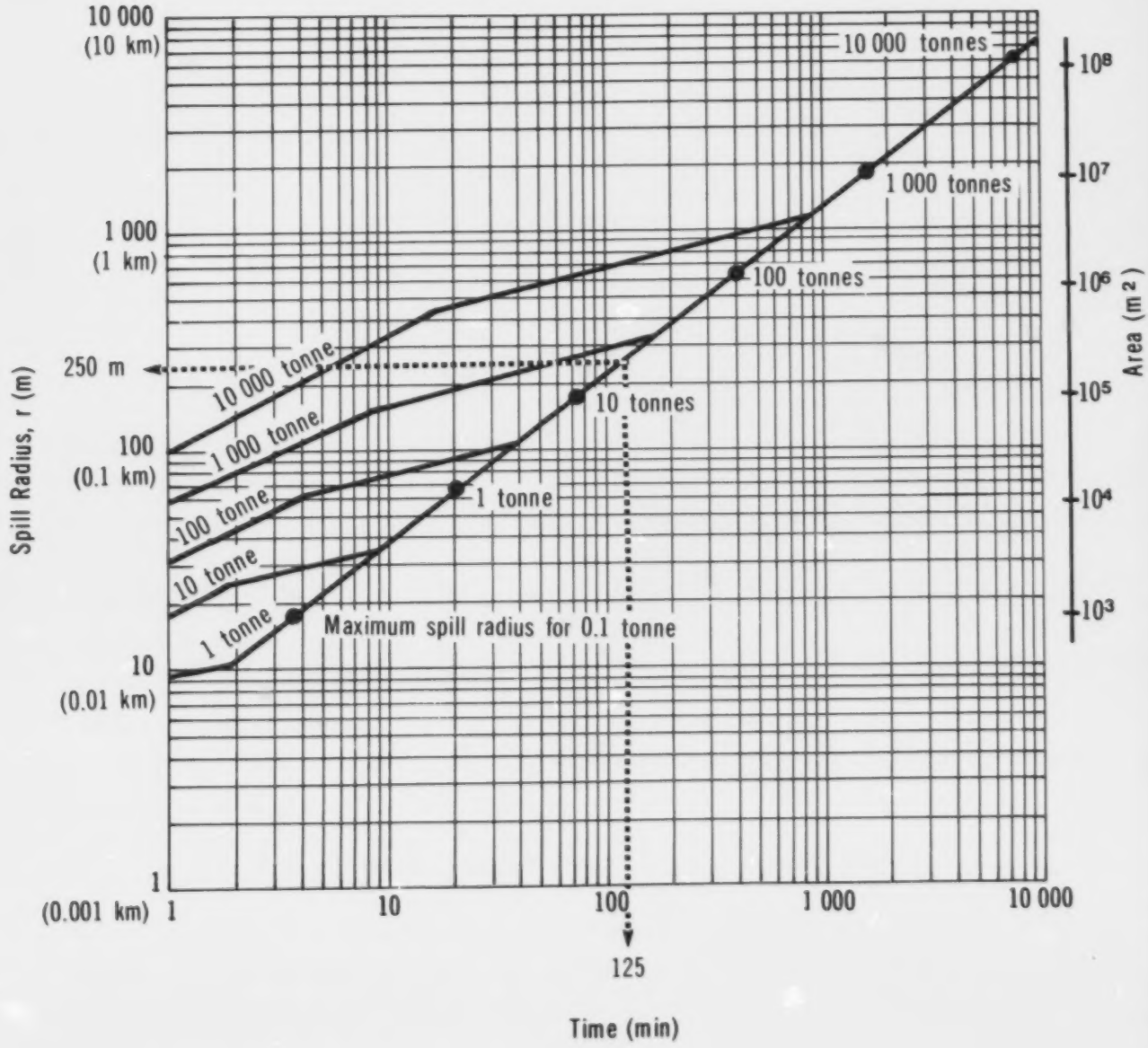


FIGURE 22

STYRENE

LENGTH OF CHANNEL AFFECTED VS SPILL RADIUS (still water - confined)

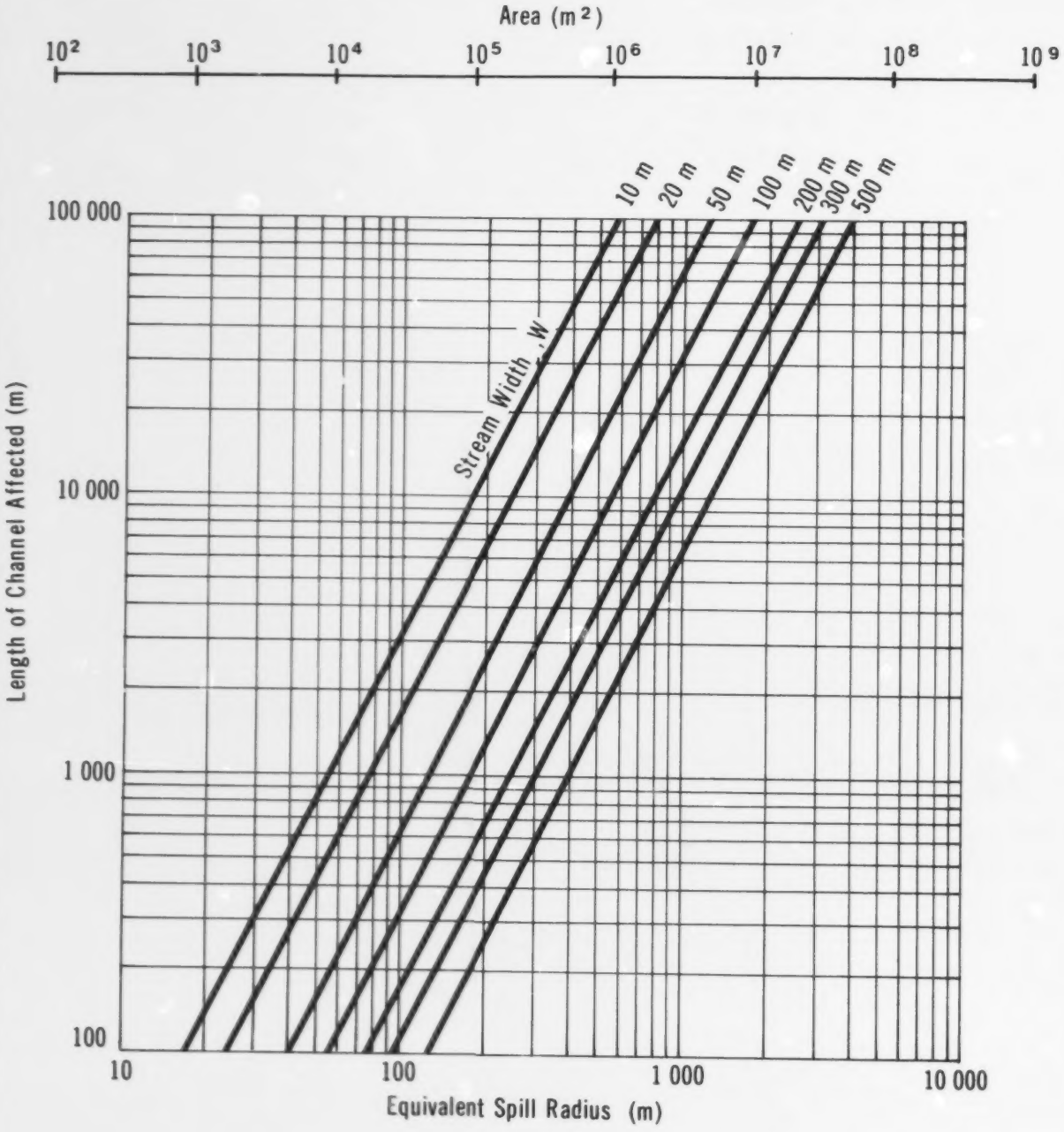
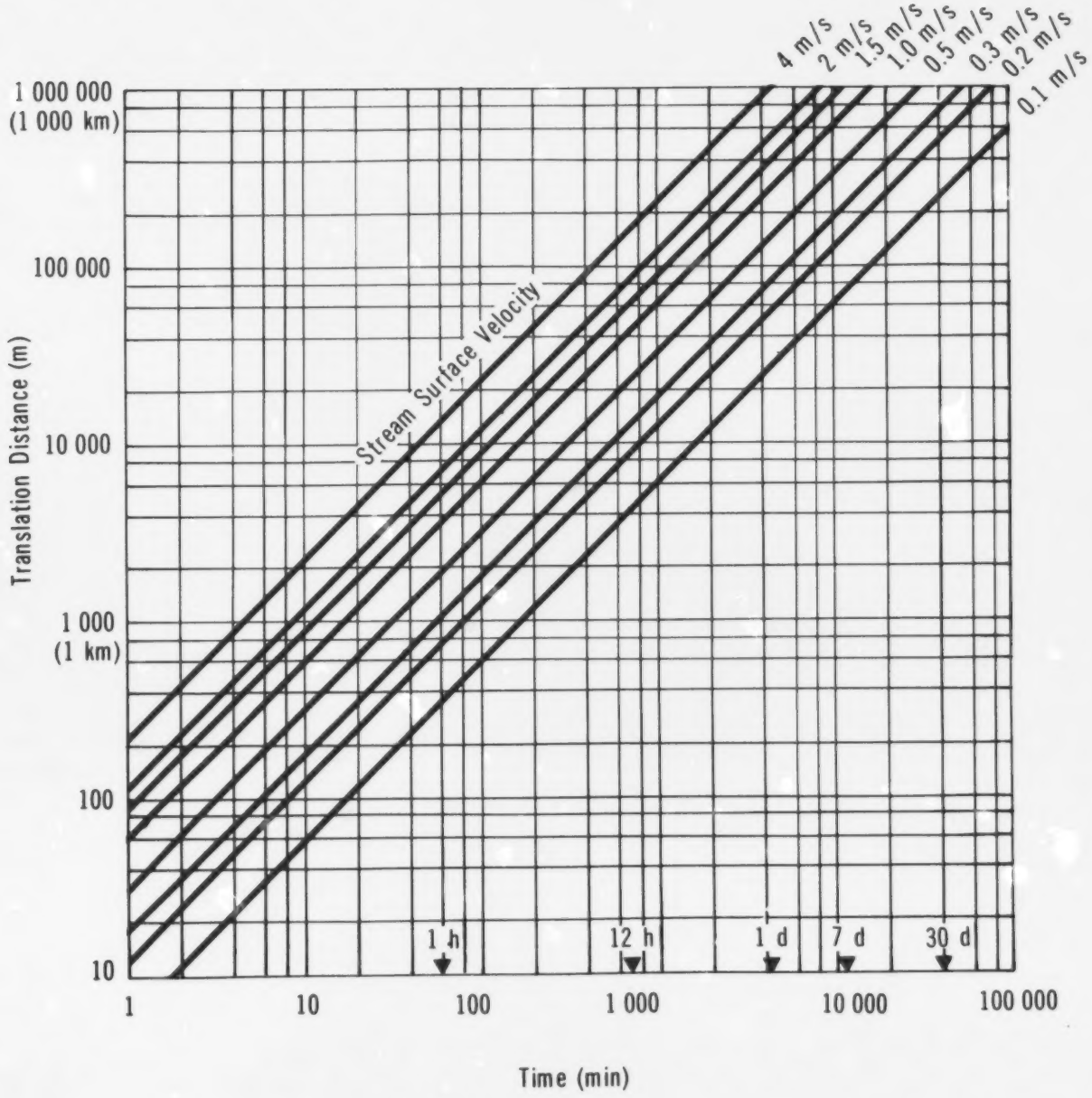


FIGURE 23

STYRENE

TRANSLATION DISTANCE (no wind)



5.4.2.4 Figure 24: Vectoral addition of surface current and wind. To take into account the effect of both wind and surface current, the spill slick is assumed to move with a velocity given by the vectoral addition of current velocity and 3 percent of the wind velocity (Raj 1974; Fingas 1979, 1980). Figure 24 is designed to simplify vectoral addition of the current and velocity components. The horizontal velocity axis is scaled for wind velocity, in km/h.

The surface current vector is added to the wind vector by determining its direction relative to the wind direction. The length of the surface current vector is defined by the vertical surface current velocity scale, in m/s. The resultant vector describes the direction and velocity the spill slick will be moving due to wind and current effects. The length of the resultant vector represents the spill translation velocity (m/s) when measured against the vertical scale.

The nomogram does not account for deformation of the slick shape when influenced by wind and/or surface currents, or for any losses which occur by evaporation or any other means.

5.4.3 Sample Calculations.

i) Problem A

A 20 tonne spill of styrene has occurred on a large lake. The wind is calm. Determine the size of the spill after 20 minutes, together with the maximum spill size and approximate time of occurrence.

Solution to Problem A

- Use Figure 21
- With t = 20 min and for a spill mass of 20 tonnes, the spill radius (r) is estimated at about 60 m by interpolation
- Similarly, the maximum spill radius (r_{max}) of about 250 m will occur in approximately 125 min (2 h)

ii) Problem B

The slick in Problem A is confined to a calm channel, approximately 50 m in width. What is the maximum length of channel affected by this spill?

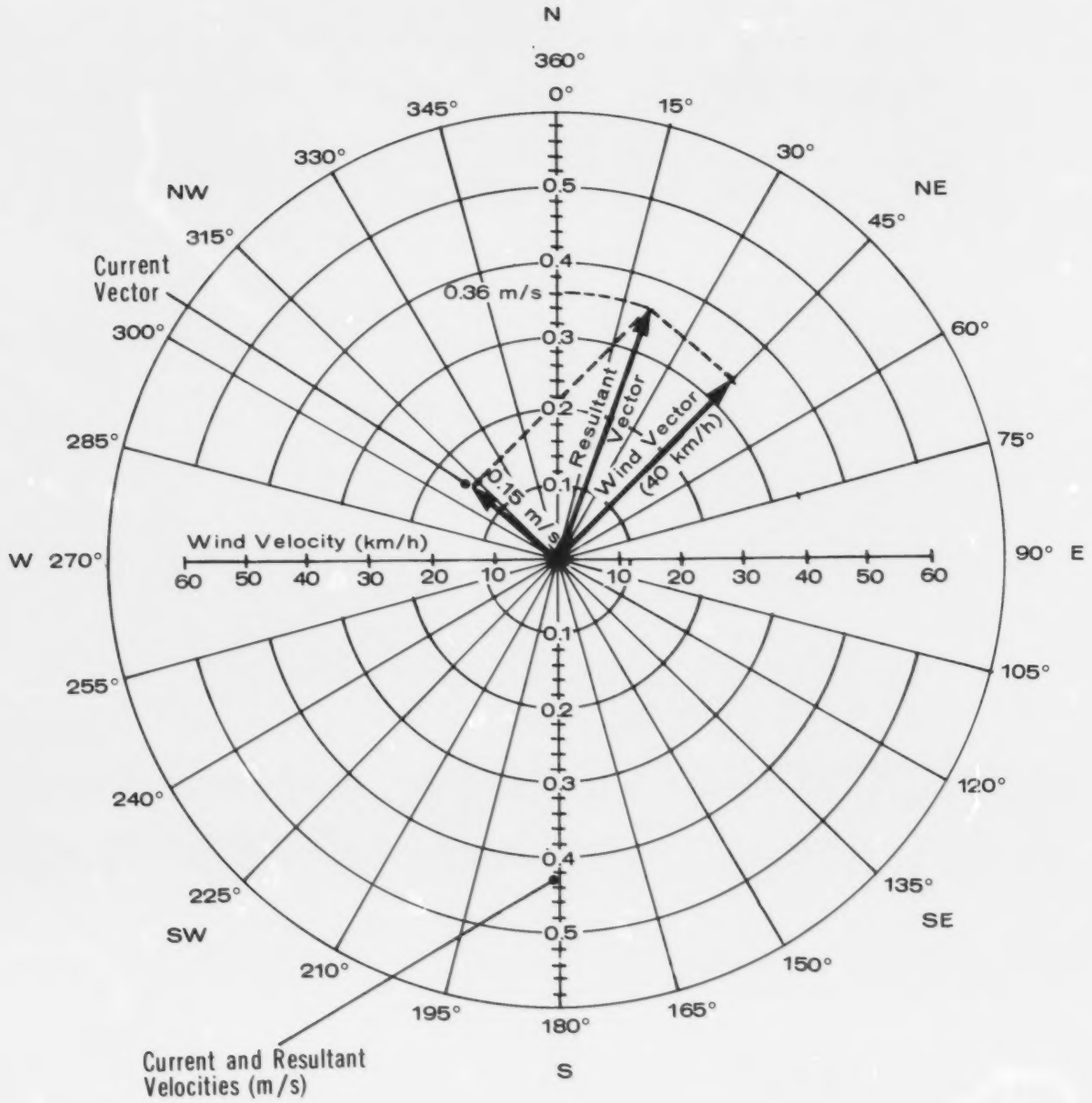
Solution to Problem B

- Figure 21 (or Solution to Problem A) gives r_{max} = 250 m for a 20 tonne spill

FIGURE 24

STYRENE

VECTORAL ADDITION OF SURFACE CURRENT AND WIND



- Use Figure 22: with r_{max} = 250 m and a stream width of 50 m, the maximum length of channel affected under still conditions is about 4000 m (4 km)

iii) Problem C

The 20 tonne spill in Problem A is being affected by a wind velocity of 40 km/h from the southwest and a surface current of 0.15 m/s at 90° from the wind direction (i.e., flow is northwest). What is the resultant direction and speed of the slick and the distance the slick has moved when it reaches its maximum size?

Solution to Problem C

Step 1: Define the wind vector

- Use Figure 24
- Determine the length of the wind vector for 40 km/h against the horizontal wind velocity scale
- Draw the wind vector at the appropriate length and in a northeasterly direction starting at the origin

Step 2: Define the surface current vector

- Determine the length of the surface current vector of 0.15 m/s against the vertical axis on Figure 24
- Draw the surface current vector at the appropriate length and in a northwesterly direction, starting from the head of the wind vector

Step 3: Define the resultant vector

- Draw the resultant vector from the origin to the head of the current vector
- Direction of translation as given by the resultant vector is about 20° east of North
- Define the translation velocity by measuring the length of the resultant vector against the vertical scale. Spill translation velocity is estimated at 0.36 m/s

Step 4: Determine the distance travelled when the spill reaches its maximum radius

- From Figure 21 (or Problem A), r_{max} = 250 m at t = 125 min (7500 s)
- Distance travelled = 7500 s x 0.36 m/s = 2700 m, by the time the spill reaches its maximum radius

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Introduction. The general principles of contaminant transport in soil and their application to this work are described in the Introduction Manual. Specific items related to styrene and the development of nomograms for it are presented below.

Styrene is relatively insoluble in water. Consequently, when spilled onto soil, its infiltration and transport downward through the soil involve multi-phase phenomena. The phases of concern are liquid styrene, water, soil, and gas or vapours.

Unfortunately, sufficient data do not exist to permit a detailed assessment of contaminant transport in a specific circumstance. A few extensive field investigations have been carried out, especially involving spills of oil, gasoline and PCBs. However, very limited information exists for styrene. Consequently, it is necessary to simplify the soil and groundwater conditions and to express contaminant behaviour through analogy to other more extensively studied materials.

A pattern for the downward movement of immiscible fluids such as styrene in soil has been prepared by comparison to oil spilled onto soil surfaces (Blokker 1971; Freeze and Cherry 1979).

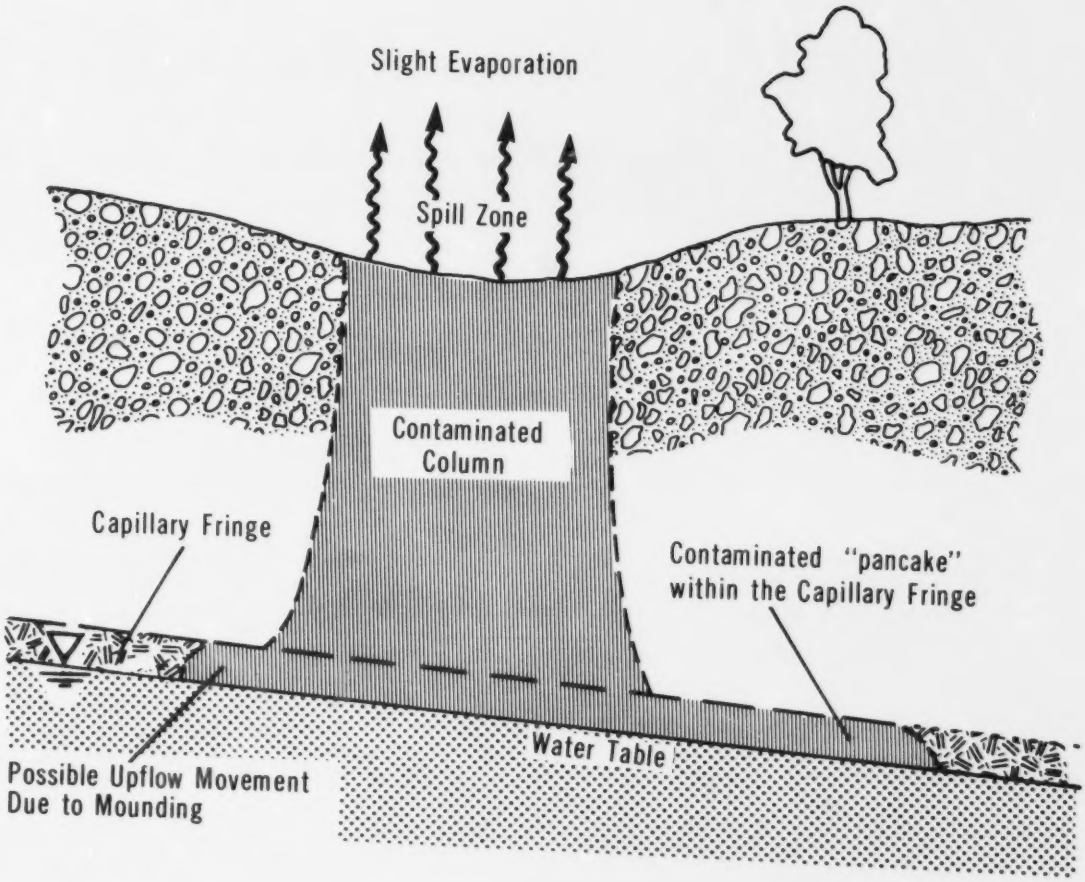
It is assumed that when the spill occurs, the soil contains water only up to its field capacity and that this condition prevails down to the groundwater table. The spilled styrene fills the pores at the soil surface and begins to penetrate downward. It is assumed that the liquid moves downward through the soil as a saturated slug, but leaving behind a constant residual amount (S_o) within the soil pores. Downward transport will continue until the volume of styrene spilled per area (B_o) equals the amount retained in the soil as S_o. Some lateral spreading may occur due to capillary action. If B_o is greater than the volume that can be retained as S_o above the groundwater table, the excess styrene will spread as a pancake within the saturated groundwater capillary fringe. The resultant contaminated zone consists of a "vertical" column and "horizontal" pancakes of soil containing the residual amount of styrene, S_o. This is shown schematically in Figure 25.

5.5.2 Equations Describing Styrene Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

FIGURE 25

STYRENE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

5.5.3 Saturated Hydraulic Conductivity of Styrene in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)

ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa•s)

g = acceleration due to gravity = 9.81 m/s^2

The appropriate properties of styrene are given in the chart below:

	Styrene	
Property	20°C	4°C
Mass density (ρ), kg/m^3	906	920
Absolute viscosity (μ), Pa•s	0.8×10^{-3}	0.9×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(1.1 \times 10^7)k$	$(1.0 \times 10^7)k$

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

	Soil Type		
Property	Coarse Sand	Silty Sand	Clay Till
Porosity (n) m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45
Residual fraction (S_o) m^3/m^3	0.05	0.1	0.2

5.5.5 Penetration Nomograms. Nomograms for the penetration of styrene into the unsaturated zone above the groundwater table were prepared for each soil. The nomograms show the total depth of styrene penetration (B) versus penetration time (t_p) for various volumes spilled per unit area of soil (B_o). Temperatures of 4°C and 20°C were

used. Calculations were based on the equations developed in the Introduction Manual. A flowchart for use of the nomograms is shown in Figure 26. The nomograms are presented in Figures 27, 28 and 29.

5.5.6 Sample Calculation. A 20 tonne spill of styrene has occurred on coarse sandy soil. The temperature is 20°C; the spill radius is approximately 8.6 m. Calculate the depth and time of penetration.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- T = 20°C
- Mass density (ρ) = 906 kg/m^3
- r = 8.6 m

Step 2: Calculate volume and area of spill

- $V = \frac{M}{\rho} = \frac{2 \times 10^4 \text{ kg}}{906 \text{ kg/m}^3} = 22.1 \text{ m}^3$
- $A = \pi r^2 = 232 \text{ m}^2$

Step 3: Calculate volumetric loading B_o

- $B_o = \frac{V}{A} = \frac{22.1}{232} = 0.1 \text{ m}^3/\text{m}^2$

Step 4: Estimate depth of penetration(B) and time of penetration (t_p)

- For coarse sand, $B_o = 0.1 \text{ m}^3/\text{m}^2$
- B = 5.7 m, t_p = 8 min

FIGURE 26

STYRENE

FLOWCHART FOR NOMOGRAM USE

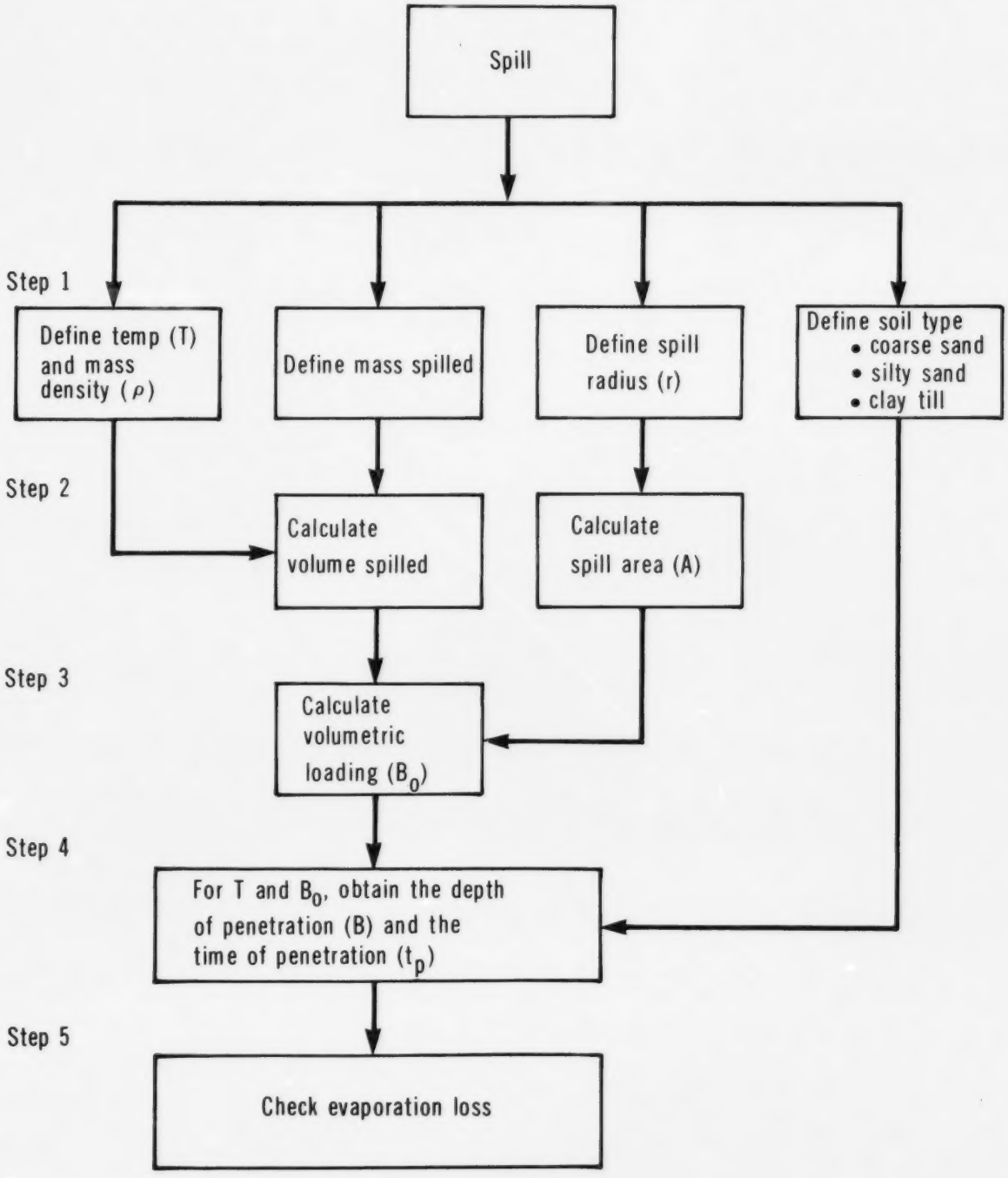


FIGURE 27

STYRENE

PENETRATION IN COARSE SAND

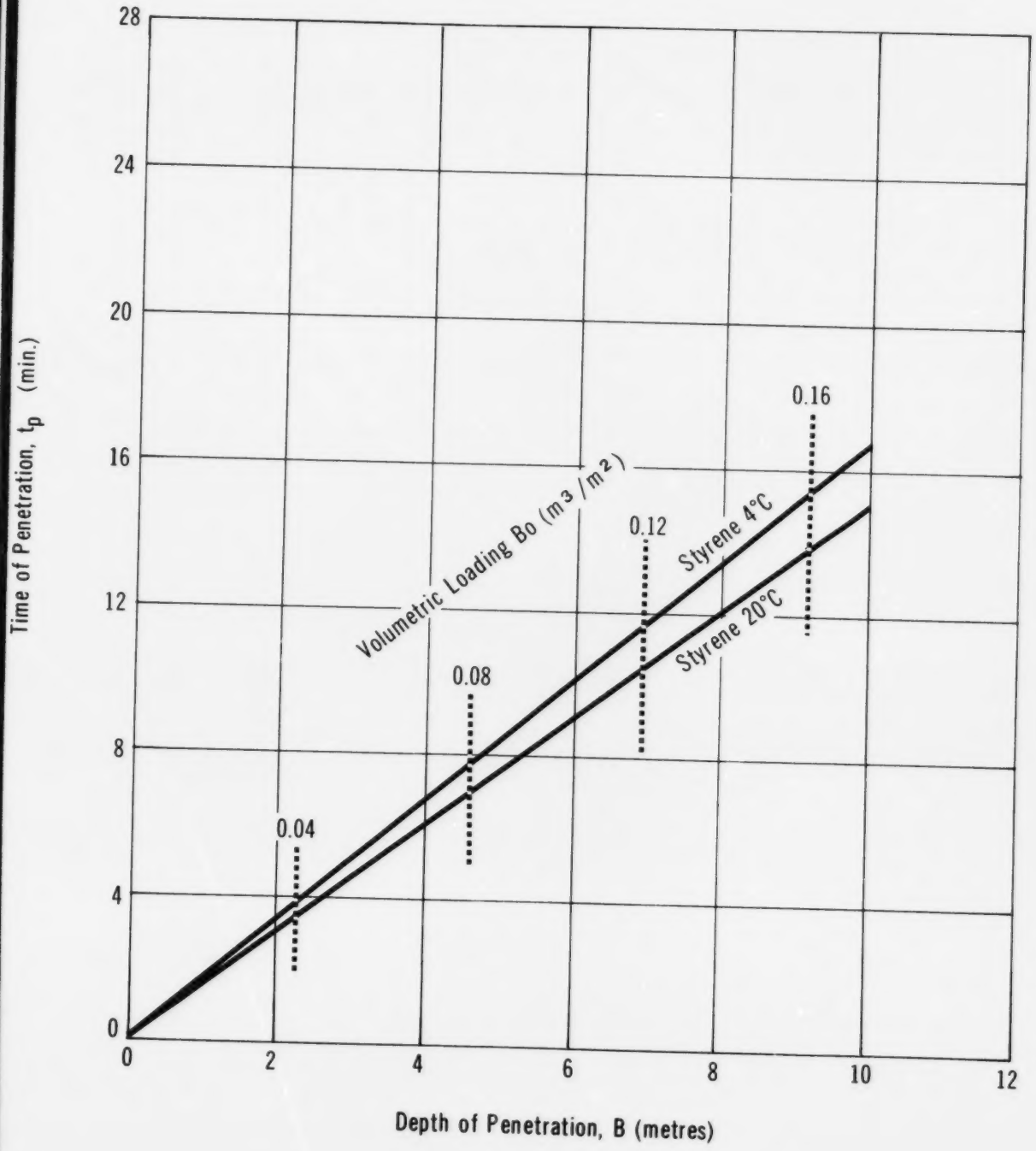


FIGURE 28

STYRENE

PENETRATION IN SILTY SAND

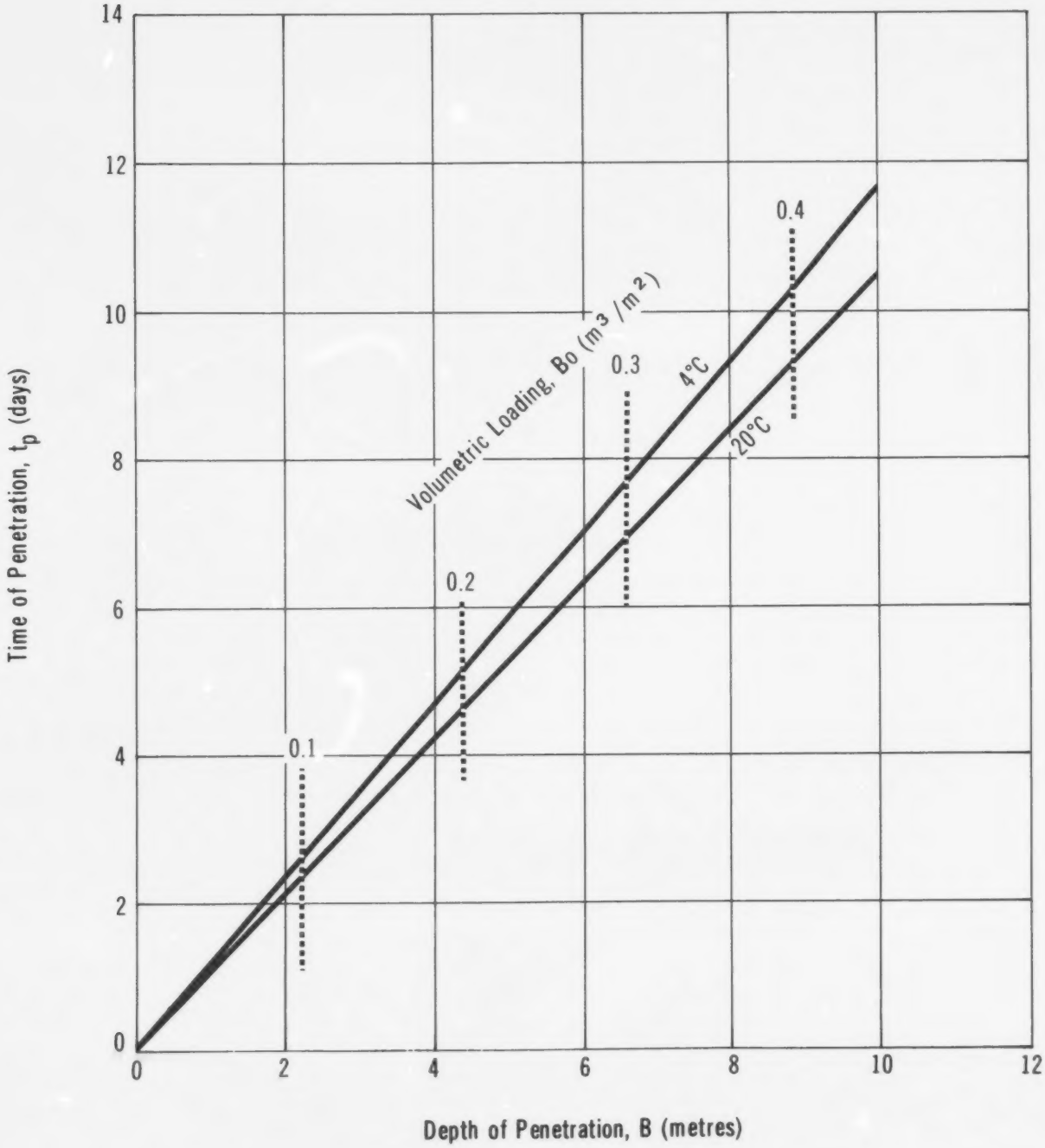
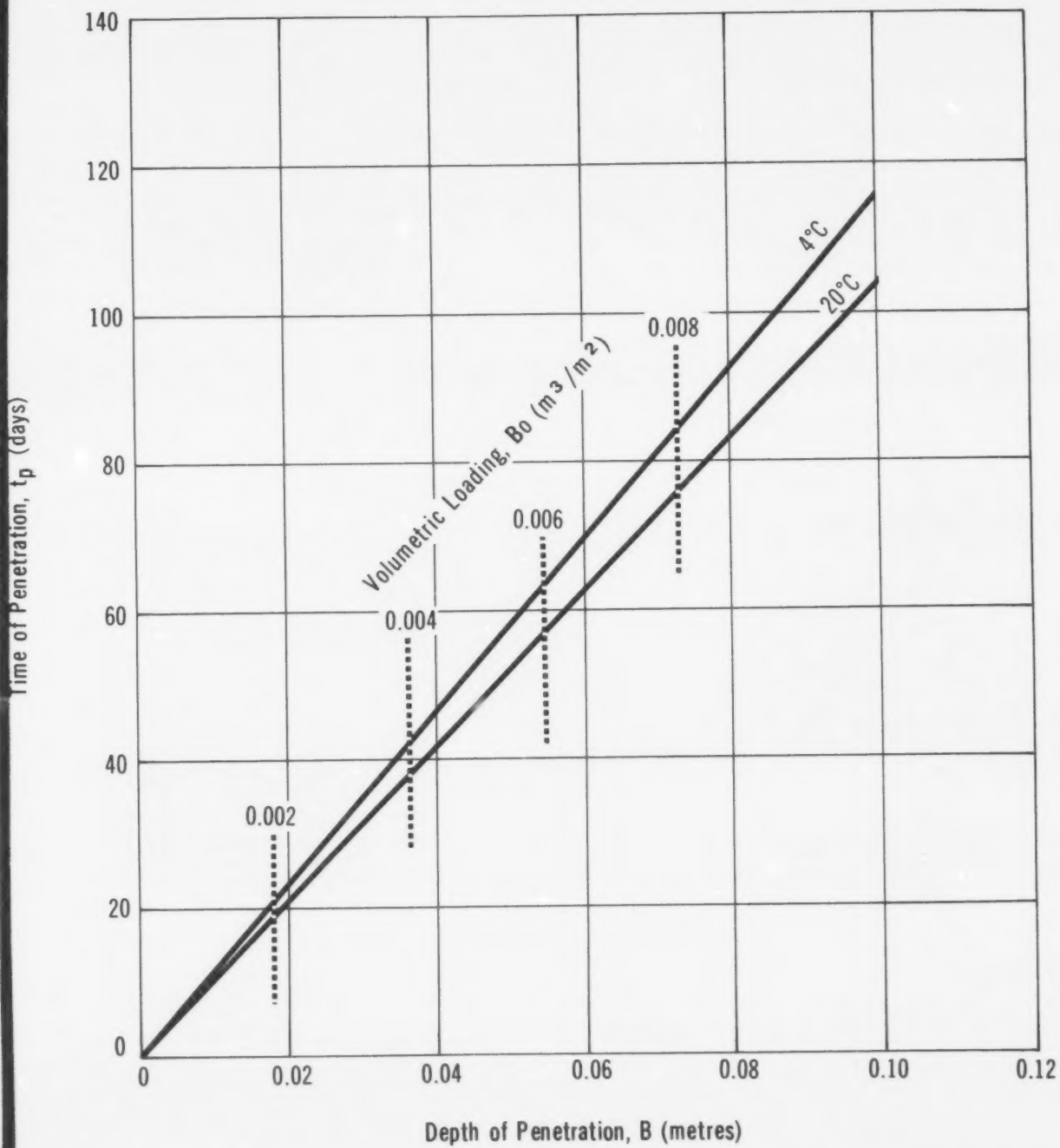


FIGURE 29

STYRENE

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. No limits specifically for styrene are in force in Canada. The approximate concentration causing an adverse taste (or tainting) in fish and other aquatic organisms is 0.25 mg/L (WQC 1972). The maximum allowable concentration (M.A.C.) of styrene in Russian surface waters is 0.1 mg/L (Verschueren 1984).

6.1.2 Air. In Ontario, the maximum permissible emission level for styrene (half-hour average) is 0.4 mg/m^3 (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 Canada. Styrene is moderately toxic to fish. The 96-hour LC_{50} rating is "less than 100 mg/L" (Water Management Goals 1978).

6.2.2 U.S. Toxicity Rating. An aquatic toxicity rating, TL_m96, of 10 to 100 ppm has been assigned (RTECS 1979).

6.2.3 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Freshwater Fish Toxicity					
26	24	Goldfish	LC_{50}	static, 10.5°C, pH 8.2	JWPCF 1980
17	tns	Dace	LD_{50}	-	Juhnke 1978
100	1	Fathead minnow	LC_{50}	Lake Superior	Mattson 1976
32	24-96	Fathead minnow	LC_{50}	Lake Superior	Mattson 1976
56.7, 53.6, 46.4	24, 48, 96	Fathead minnow	TL_m	soft, diluted, 25°C	Pickering 1966
62.8, 59.3	24, 48 96	Fathead minnow	TL_m	hard, diluted, 25°C	Pickering 1966
25.1	24-96	Bluegill	TL_m	soft, diluted, 25°C	Pickering 1966

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
64.7	24-96	Goldfish	TL_m	soft, diluted, 25°C	Pickering 1966
74.8	24-96	Guppy	TL_m	soft, diluted, 25°C	Pickering 1966
Microorganisms					
2	16	Bacteria	toxic, inhibits cell multiplication	double-distilled water, 25°C	Bringman 1980
>200	7 d	Green algae	inhibition of multiplication	double-distilled water, 27°C, 50% relative humidity	Bringman 1980
>256	72	Protozoa	inhibition of multiplication	double-distilled water, 25°C	Bringman 1980
67	tns	Blue-green algae	inhibition of cell multiplication	-	Verschueren 1984
Invertebrates					
52	24	Brine shrimp	TL_m	static	DPIMR 1981
68	24	Brine shrimp	TL_m	static	Pickering 1966
69	tns	Amphipoda	fatal in a few hours		Lindstrom 1980

6.3 Other Toxicity

Conc. (mg/kg)	Animal	Effect	Reference
46 of egg	Chick embryo	95 percent hatched; no toxic effects noted	McLaughlin 1964

6.4 Degradation

B.O.D. (w/w)	% of Theor.	Days	Seed	Method	Reference
0.55-1.95		5			Verschueren 1984
>1	65	5	sewage	fresh dilution water	Price 1974
>1	65	10	sewage	fresh dilution water	Price 1974
>1	78	15	sewage	fresh dilution water	Price 1974
>1	87	20	sewage	fresh dilution water	Price 1974
<1	8	5	sewage	salt dilution water	Price 1974
<1	18	0.4	activated sludge	treatment plant	DPIMR 1981
<1	11	36	-	CO_2 analysis	DPIMR 1981
<1	12	10	sewage	salt dilution water	Price 1974
<1	21	15	sewage	salt dilution water	Price 1974
>1	80	20	sewage	salt dilution water	Price 1974

The COD is 2.88 (w/w) and the Theoretical Oxygen Demand (ThOD) is 3.07 percent (Verschueren 1984).

6.5 Environmental Fate and Effect Studies

Pagano and co-workers (1978) exposed eggs, sperm and embryos of sea urchins (both *Paracentrotus lividus* and *Psammechinus microtuberculatus*) to 5×10^{-4} M styrene. This treatment produced signs of weak mutagenicity.

Various species of molds (*Streptomycetes*) isolated from soil and river water were subjected to 5 and 7 pecent styrene in growth culture water. Growth was attenuated in the case of the river species but not for the soil species (TAB 1981).

In another study, the addition of 100 to 500 mg/L of styrene to aqueous media containing cultures of 13 species of algae resulted in no overall effect on vitality or growth (TAB 1981).

The microbial metabolism of styrene has been briefly examined; it is postulated that styrene is converted to phenylethanol and then phenylacetic acid (TAB 1981).

6.6 Long-term Fate and Effects

Styrene accumulates in fish and produces tainting (Water Management Goals 1978). The biomagnification factor has been calculated to be 12 (Santodonato 1980). It biodegrades slowly (OHM-TADS 1981). The half-life of styrene in water (1 m depth) has been calculated to be 23.8 hours (Santodonato 1980).

7 HUMAN HEALTH

Styrene is the simplest member of the alkenyl-benzenes; it is the most prevalent of these compounds in industry. At low concentrations, it has a sweet aromatic odour; at higher concentrations, but still below the recommend exposure limits, the odour becomes disagreeable. Consequently, the compound is considered to have good warning properties (Patty 1981); however, studies have shown that there is some acclimatization to styrene odours (TAB 1981).

Acute exposure to high concentrations of styrene may produce irritation of the mucous membranes of the upper respiratory tract, nose and mouth followed by symptoms of narcosis and muscular contractions due to respiratory centre paralysis (NRC 1981). Styrene in both liquid and vapour forms is absorbed through the skin - but no more rapidly than by inhalation. The rate of absorption of the liquid through skin is 9-15 $mg/cm^2/h$ (Brighton 1979). Evidence of neurotoxicity at concentrations below 50 ppm has been reported; however, epidemiological studies of exposed workers have not reported clinically significant effects (NRC 1981). Mutagenicity and carcinogenicity testing have been completed, with inconclusive and contradictory results being reported (RTECS 1979). Teratogenicity test results using styrene have been positive.

The health effects of styrene exposure have been recently reviewed by the National Research Council (NRC 1981) and the U.S. Environmental Protection Agency (Santodonato 1980; Boyd 1981). Carcinogenesis bioassay tests conducted by the U.S. National Cancer Institute have been completed and reported (RTECS 1979). The compound has also been reported under the U.S. EPA Toxic Substances Control Act (TSCA) Inventory.

The toxicological data summarized here have been extracted from reliable standard reference sources and are representative of information in the literature. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for styrene are based upon its ability to produce lymphoid or hematopoietic tumors. The current TLV® is set at one-tenth the lowest concentration possibly causing these tumors in the positive test species, female rats (Doc. TLV 1981). Canadian provincial guidelines generally are similar to those of the USA-ACGIH unless otherwise indicated.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV• (8 h)	USA-ACGIH	50 ppm (215 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	100 ppm (430 mg/m^3	NIOSH/OSHA 1981
TWAEC (40 h/wk)	Ontario (proposed)	50 ppm (213 mg/m^3)	Ontario 1981
8 h average contamination limit	Saskatchewan	215 mg/m^3	Sask. 1981
Concentration moyenne	Québec	100 ppm (420 mg/m^3)	Québec 1979
Permissible 8 h limit	B.C.	100 ppm (420 mg/m^3)	B.C. 1980
(MAC)	Czechoslovakia	47 ppm (200 mg/m^3	Bardodej 1978
MAC	Czechoslovakia (suggested)	12 ppm (50 mg/m^3)	Bardodej 1978
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	100 ppm (425 mg/m^3)	TLV 1983
CEILING	USA-OSHA	200 ppm (850 mg/m^3)	NIOSH/OSHA 1981
PEAK (5 min/3 h)	USA-NIOSH/OSHA	600 ppm	NIOSH Guide 1978
15 min average contamination limit	Saskatchewan	425 mg/m^3	Sask. 1981
STEC (for not more than 15 min, not oftener than 4 times/d and only after 60 min have elapsed from time of previous exposure to such concentration)	Ontario (proposed)	100 ppm (425 mg/m^3)	Ontario 1981
15 min Limit	B.C.	125 ppm (525 mg/m^3)	B.C. 1980
Concentration maximale	Québec	125 ppm (525 mg/m^3)	Québec 1979

Guideline (Time)	Origin	Recommended Level	Reference
Other Human Toxicities			
IDLH	USA-NIOSH	5000 ppm	NIOSH Guide 1978
LC_{LO} (30 min)		10 000 ppm	RTECS 1979
TC_{LO}		600 ppm	RTECS 1979
TC_{LO}		376 ppm	RTECS 1979
No Effect Level		650 ppm	Patty 1981

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV®, in ppm)

At 15°C, ITI = 113

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
600 ppm (in air)	Irritation threshold, TC_{LO}	DPIMR 1981
Styrene-saturated water (1 h), hand contact	Resulted in absorption as great as 8 hours' inhalation of 12 ppm. The excretion of mandelic acid was less than after lung absorption	Doc. TLV 1981
Prolonged exposure (unspecified)	Dermatitis, defatting and dehydration of the skin	Patty 1981
Unspecified	Liquid form on the skin has been observed to result in central nervous system depression and occasional abnormalities in electroencephalograms	NIOSH Guide 1978

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
500 mg (open patch test)	Mild irritation	RTECS 1979
100 percent	Moderate irritation	RTECS 1979
10 to 20 applications (concentration unspe-	Erythema with development of a thin layer of devitalized tissue	Santodonato 1980

7.2.2 Nose and Throat Irritation.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
200 to 400 ppm (7 h in 2 periods, 20 min rest)	Widespread throat irritation, coughing	Brighton 1979
216 ppm	Nasal irritation after 20 min	Brighton 1979
99 ppm (7 h in 2 periods, 20 min rest)	Mild throat irritation in some subjects	Brighton 1979

7.2.3 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
800 ppm	Immediate irritation	Brighton 1979
376 ppm (1 h)	Some complaints within a few minutes	Brighton 1979
375 ppm (15 min)	Significant eye irritation	TDB (on-line) 1981
100 ppm (20 min)	Mild irritation	TDB (on-line) 1981
50 ppm	Irritation to some	Brighton 1979
Unspecified amount of pure liquid	Superficial transient disturbance, with return to normal within 48 h in 29 out of 30 cases	TDB (on-line) 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
1300 ppm vapour (7-8 h/d, 5 d/wk, 20 wk)	Irritation	DPIMR 1981
Undiluted	Moderate conjunctival irritation and slight, transient corneal injury	Patty 1981
18 mg of liquid	Mild irritation	DPIMR 1981
SPECIES: Rat		
1300 ppm vapour (7-8 h/d, 5 d/wk, 20 wk)	Irritation	DPIMR 1981

7.3 Threshold Perception Properties

7.3.1 Odour. Odour characteristics: Sweet at low concentrations; characteristic pungent; sharp; disagreeable (DPIMR 1981).

Parameter	Media	Concentration	Reference
Odour Threshold (Detection)	In water	0.73 ppm	ASTM 1980
Odour Threshold (Detection)	In water	37 ppm	ASTM 1980
Odour Threshold (Recognition)	In air	0.1 ppm	ASTM 1980
Odour Threshold (Recognition)	In air	0.047 ppm	ASTM 1980
Odour Threshold (Detection)	In air	0.05 ppm	ASTM 1980
Lower Odour Threshold	In air	0.02 ppm	DPIMR 1981
Upper Odour Threshold	In air	0.148 ppm	DPIMR 1981
Fatiguing	In air	52 pm (5 min) (117 ppm same results)	Brighton 1979

7.3.2 Taste. No data.

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
10 000 ppm (30 min)	LC_{LO}	DPIMR 1981
5000 ppm (1 h)	Unconsciousness	GE 1979a, b
3676 ppm	TC_{LO} - central nervous system	DPIMR 1981
1000 ppm (1 h)	Severely toxic	GE 1979a, b
800 ppm (3 h)	Immediate eye and throat irritation, increased nasal mucous secretion, metallic taste, drowsiness, vertigo. After test's termination, slight muscular weakness, accompanied by inertia and depression	Patty 1981; TAB 1981
600 ppm	Very strong odour reported, strong eye and nasal irritant	Patty 1981
200 to 400 ppm	Objectionable strong odour	Patty 1981
376 ppm (1 h)	Neurological impairment	Patty 1981
375 ppm (1 h)	Impairment of balance, manual dexterity, and muscular coordination as well as complaints of headache, nausea and eye irritation	Stewart et al. 1968. IN NRC 1981
350 ppm (30 min)	Performance on a reaction time test was impaired. No changes in performance were observed in tests of manual dexterity and perceptual speed	Gamberale and Hultengren 1974. IN NRC 1981
200, 100, or 50 ppm (1 h)	No significant objective or subjective effects	Stewart et al. 1968. IN NRC 1981
SPECIES: Guinea Pig		
5200 ppm (4 h)	Approximate LC_{50}	Patty 1981

Exposure Level (and Duration)	Effects	Reference
2820 ppm (14 h)	LC_{LO}	Spencer et al. 1942. IN NRC 1981
SPECIES: Rat		
6000 ppm (4 h)	Approximate LC_{50}	Patty 1981
5000 ppm	LC_{50}	Spencer et al. 1942. IN NRC 1981
2800 ppm (4 h)	LC_{50}	Shugaev 1969. IN NRC 1981; Harkonen 1978
SPECIES: Mouse		
5000 ppm (2 h)	LC_{50}	Shugaev 1969. IN NRC 1981
3522 ppm (2 h)	LC_{30}	Harkonen 1978
Chronic Exposures		
SPECIES: Human		
1 to 244 ppm	152 occupationally exposed workers showed increased deterioration in performance of psychomotor tests as exposure continued	Brooks et al. 1979. IN NRC 1981
150 ppm or higher (average)	A clinical study of 494 production workers revealed initial findings of acute lower respiratory and prenarcotic symptoms but normal liver function	Patty 1981
>50 ppm	Ten of the workers exposed to styrene had a mild polyneuropathy, which appeared to be related to the duration and magnitude of styrene exposure	Rosen et al. 1978. IN NRC 1981
4 kg/man/mo	Study of nine workers exposed to styrene in the use of polyester resin. Drowsiness was reported. An increase in gamma globulin was noted. One of the nine had a palpable liver, and several had slight tremors	Doc. TLV 1981

Exposure Level (and Duration)	Effects	Reference
Unspecified (1 yr, 10 yr)	Two groups of workers with two different durations of exposure. In the group exposed for 1 year, 31 out of 43 had abnormal electroencephalograms and other symptoms of CNS involvement. In a 10-year exposed group, 4 out of 18 showed abnormal results	Dolmierski et al. 1976. IN NRC 1981
Unspecified (0.5 to 14 yr)	The only significant differences between styrene-exposed and control subjects were observed in the results of the tests of visuomotor accuracy and psychomotor performance. One third of the workers having urinary mandelic acid concentrations exceeding 700 mg/L (approximately 30 ppm or (sic) a time-weighted average styrene exposure) had abnormal electroencephalograms	Lindstrom et al. 1978. IN NRC 1981
Unspecified	A study of 494 exposed workers. Prenarcotic symptoms; a distal hypoesthesia of the legs occurred in 8.5 percent of the cases. Conduction velocities of both radial and peroneal nerves were less than normal in 18.8 and 16.4 percent (respectively) of the cases. There was a consistent decrement in peroneal nerve conduction as exposure continued	Lilis et al. 1978. IN NRC 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
5 to 0.5 g/kg	LD_{50}	CHRIS 1978

Exposure Level (and Duration)	Effects	Reference
Unspecified	Slight gastrointestinal irritation, dizziness, fatigue, loss of consciousness, coma and death. If the subject recovers, there is a risk of coughing, bronchitis, fever, and pneumonia	Lefèvre 1980
Unspecified	Nausea, vomiting, and loss of appetite	AAR 1981
SPECIES: Rat		
5000 mg/kg	LD_{50}	Wolf et al. 1956. IN NRC 1981
3160 mg/kg (50/wk, 7 wk)	Survival of 3 out of 5 of males and 4 out of 5 of females, fed in corn	TAB 1981
5 mL/kg	1 death in 10 animals	Patty 1981
SPECIES: Mouse		
681 mg/kg (5 d/wk, 7 wk)	Survival of 1 out of 5 of males and females, fed in corn	TAB 1981
316 mg/kg	LD_{50}	Christensen et al. 1976. IN NRC 1981
164 mg/kg	TD_{LO}	RTECS 1979

7.4.3 Intraperitoneal.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
660 mg/kg	LD_{50}	RTECS 1979
SPECIES: Rat		
2400 mg/kg	LD_{50}	Santodonato 1980

7.4.4 Intravenous.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Mouse		
90 mg/kg	LD_{50}	RTECS 1979

7.4.5 Mutagenicity, Teratogenicity, Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
300 ppm (72 h)	Human lymphocyte cytogenic analysis has been performed. No results were reported	RTECS 1979
211 to 2 ppm or ~30 ppm (chronic)	No increase in chromosomal aberrations or sister-chromatid exchange frequency, whereas slight decrease in the mitotic index and a slight inhibition of cell growth were detected	Toxline (on-line) 1981
0.01 percent v/v or less	The cytogenic effects of styrene on human lymphocytes were reported as positive at very low concentrations	Linnainmaa et al. 1978. IN NRC 1981
"High" (hundreds of ppm)	Study of 493 styrene production workers. Clinically significant findings were rare	Lorimer et al. 1978. IN NRC 1981
Unspecified (chronic)	Significantly higher number of chromosome aberrations in 36 exposed workers (7.9 per 100 cells) compared with 37 nonexposed controls (3.2 per 100 cells)	Toxline (on-line) 1981
Unspecified	Cohort of workers engaged in styrene butadiene rubber manufacture from 1951 to 1964. From the data available, there may be a very slightly increased (relative) risk of dying due to neo-	Taulbee et al. 1976. IN NRC 1981

Exposure Level (and Duration)	Effects	Reference
	plasms of the lymphatic and hematopoietic tissues from having worked in these departments	
Unspecified	Survey of mortality among 1960 employees (in Germany) working in manufacture of styrene and polystyrene showed no increased death rate or tumor rate than general population	Frentzel-Beyme 1978
Unspecified	Case control study in a rubber manufacturing company. Strengthens the hypothesis that work experience in a synthetic rubber plant may be associated with neoplasms of the lympatic and hematopoietic tissues	Spirtas et al. 1976. IN NRC 1981
Unspecified (chronic)	Increase in rate of chromosomal aberrations in cultured lymphocytes from peripheral blood (11 to 26 percent in 10 exposed men compared with <3 percent in 5 nonexposed controls). Decondensation of chromatin and increased numbers of micronuclei and nuclear bridges were also observed	TDB (on-line) 1981
Unspecified	Induction of various cytogenetic effects. Chromosome breakage in lymphocytes in vitro	TDB (on-line) 1981
Unspecified	Negative results in exposures of styrene-polystyrene polymerization workers	Nicholson et al. 1978; Frentzel-Beyme et al. 1978. IN NRC 1981
Unspecified	Styrene has been observed to pass the placenta; some CNS defects were observed in children whose mother had been exposed to chemicals such as styrene during pregnancy	Patty 1981
SPECIES: Rat		
600 or 1000 ppm (6 h/d, 5 d/wk for most of a 2 yr period)	Combined leukemia-lymphosarcoma in female rats was 6/85 compared with 1/85 for controls	Santodonato 1980

Exposure Level (and Duration)	Effects	Reference
300 or 600 ppm (7 h/d, d 6 to 15 of gestation)	Decrease in embryo length and a few minor skeletal deformities at 600 ppm, but not at 300 ppm	Santodonato 1980
SPECIES: Rat		
0.4 to 12 ppm (4 h/d, throughout gestation)	Decreased number of offspring and a lowered viability of newborns	Santodonato 1980
1350 mg/kg/wk (100 wk)	Weak evidence of carcinogenicity by slight increase in tumor incidence	Ponomarkov 1978
SPECIES: Mouse		
250 or 300 ppm (6 h/d during major organogenesis of pregnancy)	Embryotoxicity was raised, and some minor skeletal malformations were noted in mice, but not in Chinese hamsters under similar experimental conditions	Toxline (on-line) 1981
1 g/kg	Positive test using host-mediated assay with *Saccharomyces cerevisiae*	RTECS 1979
100 mM (millimoles)	On a forward mutation system of *Schizosaccharomyces pombe*, P1 strain fortified with mouse liver, negative results	Loprieno et al. 1976, 1978. IN NRC 1981
1350 mg/kg/wk (100 wk)	Weak evidence of carcinogenicity by increased incidence of liver tumors	Ponomarkov 1978
SPECIES: Hamster		
17 mM (millimoles)	Negative on forward mutation in Chinese hamster cells, (V79 strain)	NRC 1981
SPECIES: Salmonella		
Unspecified	Evidence of mutagenicity in Ames assay	Meester et al. 1977; Roberfroid et al. 1978; Vainino 1978; Vainio et al. 1976; Watabe et al. 1978. IN NRC 1981
Unspecified	No evidence of mutagenicity in Ames assay	Busk 1979; Milvy and Garro 1976. IN NRC 1981

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Increased nasal mucus secretions.
2. Throat irritation.
3. Nausea.
4. Headache.
5. Drowsiness, fatigue.
6. Rapid breathing (Lefèvre 1980).
7. Impaired reaction time (Gamberake and Hultengren 1974. IN NRC 1981).
8. Depression (Patty 1981).
9. Muscular weakness (Patty 1981).
10. Neurological impairment (Patty 1981).
11. Mental confusion (Lefèvre 1980).
12. Impaired manual dexterity and muscular coordination (Stewart et al. 1968. IN NRC 1981).
13. Depression of the central nervous system.
14. Unconsciousness.
15. Convulsions.
16. Death.

7.5.2 Ingestion.

1. Slight gastrointestinal irritation (Lefèvre 1980).
2. Dizziness.
3. Fatigue.
4. Loss of consciousness.
5. Coma.
6. Death.

7.5.3 Skin Contact.

1. Defatting and dehydration (Patty 1981).
2. Dermatitis (Patty 1981).
3. Central nervous system depression (NIOSH/OSHA 1981).

7.5.4 Eye Contact.

1. Irritation.
2. Stinging sensation.
3. Watering eyes.
4. Conjunctival irritation (Patty 1981).

7.6 Metabolism of Styrene

The metabolism of styrene (whether ingested or inhaled) has been partially determined by experiments with rats and mice as well as by test on humans (Bardodej 1978; TAB 1981; Brighton 1979). The metabolic transformations known or suspected to occur are shown in Figure 30. Results from a variety of tests have shown that styrene is largely excreted in the urine as mandelic acid. In fact, tests for mandelic acid are used to determine styrene exposure and have been proposed as a test to determine industrial exposure (Bardodej 1978). In one test, 22 ppm styrene was administered to humans over an 8-hour period. Tests showed that 61 percent of the vapour was retained in the respiratory tract; of the dose that was retained, 85 percent was excreted in the urine as mandelic acid and 10 percent as phenylglyoxylic acid (Santodonato 1980). In other tests, the half-lives of styrene in the body (before excretion of metabolites) was determined to be about 15 h for a 60 ppm, 6 h, dose and 20 h for a 600 ppm, 6 h, dose (Santodonato 1980). The toxicity of most of the metabolites is low. The following is a partial list (Bardodej 1978):

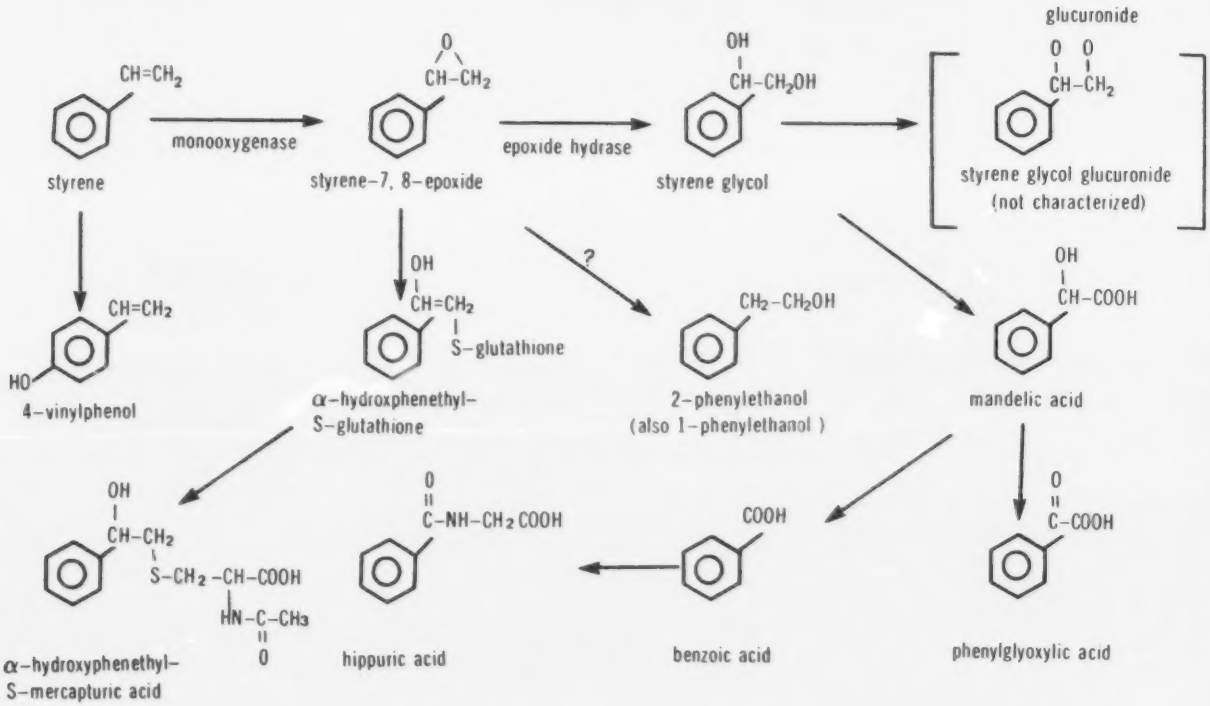
Metabolite	LD_{50} to rat (orally) (mg/kg)
Styrene	4920 to 5840
Styrene 7,8-epoxide	2830 to 4290
2-Phenylethanol	400 to 1790
Mandelic acid	3000 (lethal dose)

FIGURE 30

STYRENE

METABOLIC PATHWAYS

Reference: TAB 1981; BARDODEJ 1978



8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Styrene (Monomer) with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Fire		•												Sax 1979
Heat				•									May self-polymerize at elevated temperatures	Bretherick 1979
SPECIFIC CHEMICALS														
Butyllithium			•	•									Will catalyze polymerization	Bretherick 1979
Chlorosulphonic Acid	•						•						In a closed container	NFPA 1978
Dibenzoyl Peroxide				•									Runaway polymerization	Bretherick 1979
Ferric Chloride and Chlorine Gas				•									Catalyzes polymerization in a closed container	Bretherick 1979
Oleum	•						•							NFPA 1978
Oxygen		•							•				Violent explosion on heating	Bretherick 1979
Sulphuric Acid	•						•						In a closed container with 96 percent H_2SO_4	NFPA 1978

8.1 Compatibility of Styrene (Monomer) with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
CHEMICAL GROUPS														
Alkali Metal-graphite Compounds					•								Will initiate polymerization	Bretherick 1979
Azo Compounds					•									EPA 600/2-80-076
Caustics	•				•									EPA 600/2-80-076
Explosives		•												EPA 600/2-80-076
Mineral Acids	•				•									EPA 600/2-80-076
Nitrides	•				•									EPA 600/2-80-076
Oxidizing Acids	•				•	•								EPA 600/2-80-076
Oxidizing Agents	•	•								•				EPA 600/2-80-076
Reducing Agents	•		•		•									EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Styrene is a flammable liquid. Vapour forms explosive mixtures with air and may travel along surfaces to ignition sources and flash back. When heated, polymerization may take place; if this occurs in a container, there is possibility of violent rupture of the container (NFPA 1978). Polymerization may also occur if styrene is exposed to light or catalytic materials, or if the inhibitor is exhausted or removed (GE 1979a, b).

9.1.2 Fire Extinguishing Agents. Shut off leak before attempting to extinguish. Use water spray to cool containers involved in a fire to prevent rupture.

Small fires: Dry chemical, CO_2, water fog or foam.

Large fires: Water spray, fog or foam.

Move containers from fire area if this can be done without risk. Stay away from tank ends. For massive fires, use unmanned hose holder or monitor nozzles (ERG 1980). Water should be used sparingly on smaller fires as it will spread liquid styrene (DPIMR 1981).

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact or inhalation (GE 1979a, b). Use water spray to reduce vapours (ERG 1980), and to protect men attempting to stop a leak (NFPA 1978). Application of fluorocarbon water foam to diminish vapours should be considered (EPA 670/2-75-042).

The following absorbent materials have shown possible applicability for vapour suppression and/or containment of styrene: cellosize and hycar (ICI 1972).

9.1.3.2 Spills on land. Contain if possible by forming mechanical or chemical barriers to prevent spreading. Absorb spilled material with sand or vermiculite and shovel into containers for disposal. Attempted reclamation of styrene spills is not usually recommended (GE 1979a, b; EPA 670/2-75-042). Application of fly ash or cement powder to absorb the liquid bulk should also be considered (EPA 670/2-75-042). Other recommended collecting materials are polypropylene and cellulose fibres (CG-D-38-76). Sorbents used should preferably be noncombustible.

9.1.3.3 Spills on water. Contain if possible with booms or natural barriers to limit spreading. Remove trapped material with suction hoses or (oil) skimming equipment (EPA 670/2-75-042).

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills on land. If the spilled material has been contained in a holding area, suction equipment and/or sorbent foams can be used to remove the slick (OHM-TADS 1981).

9.1.4.2 Spills on water. After containment of spilled material with booms, (oil) skimming equipment and/or sorbent foams can be used to remove the slick (OHM-TADS 1981). If solubilized in water, apply activated carbon at 10 percent the spill amount over the region occupied by 10 mg/L or greater concentrations (EPA 670/2-75-042).

9.1.4.3 General. For treatment of contaminated water, gravity separation of solids followed by skimming of surface to remove spilled material is recommended. If skimming is not sufficient, dual-media filtration followed by carbon adsorption should be considered. Recommended carbon ratio: 1.0 kg to 10.0 kg soluble material. The wastewater from backwash of the filtration and adsorption units is returned to the gravity separator (EPA 600/2-77-227).

The following treatment processes have shown possible applicability for spill countermeasures:

Process	Percent Removal (TSA 1980)	Process	Maximum Percent Removal (EPA 600/8-80-042E)
Biological	70 to 100	Solvent Extraction	>93
Stripping	98 to 99	Carbon Adsorption	55 to 97

9.1.5 Disposal. Waste styrene must never be discharged directly into sewers or surface waters. The material can be burned in an incinerator (GE 1979a, b). Contaminated water may be made safe for disposal by removal to a safe location where the mixture may be blown with air. The outlet air stream should be burned in cases of gross contamination (MCA 1971).

9.1.6 Charcoal Filtration Data (EPA 600/8-80-023). The following recommended values for the removal of styrene in water by either the single stage powdered carbon contactor or the granular carbon column adsorption system were obtained using the Freundlich Adsorption equation. The derivation of the equation is discussed in the Introduction Manual:

SINGLE STAGE POWDERED CARBON CONTACTOR SYSTEM

Initial Concentration (mg/L)	Carbon Doses (mg/L)	Final Concentration (mg/L)
1.0	27	0.1
1.0	110	0.01
1.0	400	0.001
0.1	9.8	0.01
0.1	39	0.001
0.01	3.6	0.001

GRANULAR CARBON COLUMN SYSTEM (ESTIMATED)

Initial Concentration (mg/L)	Carbon Doses or Requirements to Achieve Breakthrough Doses (mg/L)
1.0	8.3
0.1	3.0
0.01	1.1

9.1.7 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spill material is known to be styrene:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid styrene (NIOSH/OSHA 1981).
- The following clothing material showed breakthrough times of greater than 1 hour: polyvinyl alcohol. The following showed breakthrough times of approximately 1 hour: polyethylene, Viton. The following showed breakthrough times of less than 1 hour: butyl rubber, natural rubber, neoprene and PVC (Little 1983).
- Splash-proof and chemical safety goggles are also recommended for eye protection (NIOSH/OSHA 1981; GE 1979a, b).
- Nonimpervious clothing which becomes contaminated with liquid styrene should be removed promptly and not reworn until the styrene is removed from the clothing (NIOSH/OSHA 1981). Contaminated leather shoes and clothes should be destroyed (CCPA 1983).
- Chemical resistant synthetic rubber is recommended for boots (MCA 1971).
- Eye wash stations and safety showers should be readily available in areas of use and spill situations (GE 1979a, b).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where styrene is present (NIOSH/OSHA 1981):

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapour Concentration 400 ppm or less	Any chemical cartridge respirator with an organic vapour cartridge(s).**
	Any supplied-air respirator.**
	Any self-contained breathing apparatus.**
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapour cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapour canister.
	Any supplied air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapours.
	Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.
** If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

9.1.8 Storage Precautions. Store in tightly closed, mild steel containers in a well-ventilated area away from heat and ignition sources, direct sunlight, oxidizing agents, and polymerization catalysts. Store in the original container to avoid contamination. Monitor inhibitor content and polymer formation in stored styrene. Large tankage should be inerted with nitrogen. Complete elimination of oxygen will lead to depletion of dissolved oxygen in the liquid monomer and the TBC inhibitor becomes rapidly ineffective. When nitrogen is used, the monomer should be aerated once a week for about 30 minutes or until the oxygen level again reaches saturation (Dow 1981). Carry out transfers with grounded and bonded containers. No smoking in areas of storage, handling or use. Inhibited styrene can polymerize from frictional heat in a running centrifugal pump if flow is stopped. Condensed styrene vapours (no inhibition) can polymerize (GE 1979a, b).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment,

materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study.

Recovery from Water - Floating Materials	Amine Carbamate Gelling Agent and Application System
Treating Agents	Hazorb (Sorbent)

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill responses and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency or spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.1 General

A number of spill accidents for this chemical have been documented. The incident discussed here has been selected primarily because significant information, potentially useful in future spill circumstances, has been learned from it.

10.2 Train Derailment (HMIR 1980)

In a train derailment which occurred at 2:00 a.m. in an urban area, two tank cars each carrying approximately 76 000 L of styrene monomer were damaged and spilled some of their contents. It was estimated that most of the spilled product, approximately 19 000 L, came from a 7.5 cm hole in one of the cars. Emergency personnel evacuated about 8600 people from an area approximately 1.5 km by 3 km around the spill site. Orders were also issued to shut down local gas and electric power service.

Fire fighters arrived at the spill site and immediately sprayed water on the styrene tank cars to dissipate the vapours and minimize the danger of an explosion. Water spraying continued for a period of 5.5 h; 1.1 million L of water were used.

When wreck-clearing crews arrived at the site, fire fighters began applying "3M LIGHT WATER AQUEOUS FILM FORMING FOAM" to the cars to increase vapour suppression and/or containment. Response crews built two siphon dams on a nearby creek where contaminated water was collecting. Approximately 132 000 L of water and styrene monomer were pumped from behind the dams into tank trucks. By late afternoon, all evacuees were allowed to return to their homes, with the exception of seven families whose homes bordered the spill site. Five individuals who suffered from nausea and respiratory irritation were treated and released from local hospitals.

Cleanup crews, equipped with protective clothing and MSA respirators, used soft cedar shingles and plastic bonding materials to patch the hole in the damaged tank car. A Bendix Model 1314 Gastechtor was used to monitor the air concentration of the styrene monomer while the crew were applying the patch. The tank car was repositioned

to remove pressure from the patched hole. Response personnel then used Pacer chemical pumps to transfer the remaining styrene monomer into two 34 000 L tank trucks. The off-loading operation was completed by early morning of the next day.

Air monitoring around the spill site indicated that the concentration of styrene monomer in the air had decreased from about 100 to 10 ppm during a 1 day period. On the third and fourth day after the incident, the remaining families were allowed to return to their homes. At this time, soil and air monitoring at ground level indicated that 15 to 30 cm of topsoil in different areas of the spill site were contaminated with styrene monomer. On the next day, the contaminated soil was removed and disposed of to a sanitary landfill. The ground was allowed to air for a period of 24 hours and a new layer of topsoil was applied to the areas where contaminated soil has been removed.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Styrene in Air

11.1.1 Gas Chromatography (NIOSH 1977). A range of 426 to 1710 mg/m^3 (100 to 402 ppm) of styrene in air may be determined by gas chromatography using flame ionization detection.

A known volume of air is drawn through a 7 cm x 6 mm O.D. charcoal tube containing 2 sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The first section contains 100 mg whereas the second section contains 50 mg. A silylated glass wool plug is placed before the front absorbing section. A sample size of 5 L collected at a flow rate of 1 L/min is recommended.

The charcoal tube sample is scored before the first section of charcoal and broken. The larger section of charcoal is transferred to a 1 mL stoppered sample container containing 0.5 mL of carbon disulphide. The same operation is performed with the back-up section. The samples should be allowed to desorb for 30 minutes. A 5 µL aliquot of sample is injected into a gas chromatograph equipped with a flame ionization detector.

Typical gas chromatograph conditions are: nitrogen carrier gas flow at 50 mL/min, hydrogen gas flow at 65 mL/min, air flow at 500 mL/min, injector temperature at 195°C, detector temperature at 255°C, and a column temperature of 109°C. The column is a 10 foot, 1/8 inch O.D. stainless steel column packed with 10 percent FFAP (free-fatty acid packing) on acid-washed DMCS (dimethyl chlorosilane) chromosorb W.

The styrene is determined using an electronic integrator which measures area under the peak in conjunction with a standard curve.

11.2 Qualitative Method for the Detection of Styrene in Air

Styrene in air may be determined qualitatively using a Drager detection tube for styrene. Air is drawn through a Drager detection tube using a Drager multi-gas detector pump. A colour change on the indicating layer from white to yellow indicates styrene. The color change is based on the reaction between styrene and sulphuric acid (Drager 1979).

11.3 Quantitative Method for the Detection of Styrene in Water

11.3.1 Partition Infrared (AWWA 1981). A range of 40 to 400 ppm (40 to 400 µg/mL) of styrene in water may be determined by partition infrared spectrophotometry.

A minimum of 1 L of a representative water sample is collected in an appropriate container. The sample is acidified to pH 2 by the addition of approximately 5 mL of 50 percent hydrochloric acid. The sample is then transferred to a separatory funnel and the sample container is rinsed with 30 mL of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane). The solvent rinse is added to the separatory funnel. The solvent layer is drained into a 100 mL volumetric flask. The aqueous layer is extracted with two or more 30 mL portions of solvent. The solvent extracts are combined in the volumetric flask and the volume taken to mark with solvent.

The styrene is determined using 1 cm matched near-infrared silica cells and a double-beam recording IR spectrophotometer in conjunction with a standard curve. The sample is scanned from 3200 cm^{-1} to 2700 cm^{-1}, with solvent in the reference beam.

11.4 Qualitative Method for the Detection of Styrene in Water

The sample is collected as in Section 11.3.1 and extracted. A suitable portion of sample is treated with hydrogen peroxide and formic acid followed by potassium permanganate. The formation of a precipitate indicates the presence of styrene. If a more positive identification is needed, the acid derivative is isolated and its melting point determined (Morrison 1976). A very simple method is to take a sample of water and heat

to 40°C or more and use a Drager tube to detect styrene in the vapour space (CCPA 1983).

11.5 Quantitative Method for the Detection of Styrene in Soil

11.5.1 Infrared Spectrophotometry (AWWA 1981). A range of 40 to 400 ppm (40 to 400 µg/mL) of styrene in soil may be determined using infrared spectrophotometry.

Approximately 20 g of soil, accurately weighed, is collected in a glass jar and dried by the addition of magnesium sulphate. A 30 mL volume of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the styrene from the soil. Using 1 cm matched quartz cells with Freon® 113 in the reference beam of a double-beam IR recording spectrophotometer, the sample is scanned from 3200 cm^{-1} to 2700 cm^{-1}. The styrene is determined using a calibration curve.

11.6 Qualitative Method for the Detection of Styrene in Soil

The sample is collected as in Section 11.5.1 and extracted. A suitable portion of sample is treated with hydrogen peroxide and formic acid, followed by potassium permanganate. The formation of a precipitate indicates the presence of styrene. If a more positive identification is needed, the acid derivative is isolated and its melting point determined (Morrison 1976). A simple method is to heat a soil sample to 40°C or more and use a Drager tube to detect styrene in the vapour space (CCPA 1983).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/ alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight